Structure and dynamics of complex hydrogen-bonded systems

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Chapter 7

Elucidating the mechanism of a rotaxane-based molecular machine using time-resolved UV-IR spectroscopy

We have shown in Chapters 3 and 6 that 2D-IR and photon-echo peak-shift spectroscopy are methods that allow us to study the molecular structure and dynamics of man-made molecular devices. However, these chapters focused on the equilibrium structure and fluctuations. Since our main goal is to study the mechanical motion within molecular machines, we need a tool that gives us the capability to observe the molecular structure in non-equilibrium states. This means that we need to be able to trigger the molecular motion and detect structural changes on a nanosecond time scale. Time-resolved UV-IR spectroscopy is an experimental method that fulfills both these demands.

In this Chapter, we report the first results of time-resolved UV-IR pump-probe experiments on a light-triggered molecular machine based on the rotaxane architecture described in the previous chapter. The intramolecular motion of the rotaxane, shown in Fig. 7.1, can be triggered by either electrochemical or photochemical reduction of the naphthalimide station (ni, shown in red) to its radical anion form (ni−). In the neutral molecule, the macrocycle (mc, blue in Fig. 7.1) resides predominantly on the succinamide station (succ, green in Fig. 7.1). The NH groups of the mc are hydrogen-bonded to the CO groups of the thread. After excitation of the ni station with 355 nm light, the rotaxane undergoes rapid intersystem crossing (τISC = 1.6 ns) from the singlet to the triplet state. The triplet state rapidly decays with a lifetime of ~30 ns due to the electron transfer. During this process, the ni station is reduced by the electron donor, 1,4-diazabicyclo[2.2.2]octane...
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(DABCO), to form a radical anion (ni⁻). The ni⁻ station has a much larger affinity for the mc than the succ station. Consequently, the macrocycle will travel over the thread (black in Fig. 7.1) and form hydrogen bonds with the ni⁻ station. Charge recombination between the radical anion of the rotaxane and the radical cation of the electron donor occurs within ~30 µs. The ni station returns to being a poor hydrogen-bond acceptor in comparison to the succ station, the macrocycle travels back over the thread, binds to the succ station, and the system is ready to shuttle again. This process was previously observed using UV-VIS time-resolved absorption spectroscopy. However, the absorption of the ni⁻ species used as a probe in this study has only a limited sensitivity to structural changes. Steady-state spectro-electrochemical experiments in the IR have been performed on the same ro-

\[ \text{Figure 7.1: Chemical structure of the rotaxane system in the neutral and shutttled radical anion state. The labeled CO groups correspond to the labeled peaks in Fig. 7.5.} \]
taxane system by Jagesar et al.\textsuperscript{19} The spectra of both co-conformers were observed but the transition between the two cannot be followed with this technique. Here, the experimental technique combines structural (IR) and temporal (ns) resolution. By investigating the dependence of the dynamics on temperature and device length with a probe that is sensitive to local structure, we have elucidated the elementary steps of the shuttling mechanism.

7.1 Materials and methods

In our time-resolved UV-pump IR-probe experiments, we employ the UV-IR pump probe setup described in Section 2.3.7. A nanosecond UV pulse excites the naphthalimide station and thus triggers the shuttling of a rotaxane. The mid-IR probe pulse is used to observe the subsequent vibrational absorption changes. The synthesis and purification of rotaxanes have been described in detail elsewhere.\textsuperscript{3,118} All experiments are carried out on a mixture of 0.1 mM solution of the rotaxane and 0.01M solution of DABCO in deuterated acetonitrile (MeCN-d\textsubscript{3}). The sample is kept in a 11 mm thick demountable IR sample cell with 2 mm thick CaF\textsubscript{2} windows. To minimize the photobleaching caused by the UV pump, we flow the solution using a pump with teflon tubing and fittings. We also need to avoid water due to the absorption of the H\textsubscript{2}O bending mode at 1650 cm\textsuperscript{-1}, and because water might disrupt the hydrogen-bonding link between the macrocycle and thread. Additionally, we bubble the sample with argon for approximately 15 minutes to remove oxygen from solution. Oxygen contamination causes a rapid quenching of the triplet state of the ni station that results in the absence of electron transfer. In that case, no ni\textsuperscript{-} is formed and the shuttling process does not occur.

7.2 Results and discussion

7.2.1 Steady-state Spectra

In this Chapter, rotaxanes with a track length \(n\) will be referred to as C\textsubscript{n}. The solvent-subtracted steady-state absorption spectrum of the C\textsubscript{12} rotaxane is shown in Fig. 7.2. The steady-state absorption spectra of rotaxanes with different carbon-chain lengths are very similar. This is to be expected, since the only structural difference between the rotaxanes is the number of CH\textsubscript{2} units between the stations. The peaks observed in the steady-state absorption and difference absorption spectra (Fig. 7.5B) have been assigned by Jagesar \textit{et al.}\textsuperscript{19} using steady-state absorption spectra and spectro-electrochemistry on the rotaxane and its separate components. The peaks observed at 1701 cm\textsuperscript{-1} and 1662 cm\textsuperscript{-1} are assigned to the symmetric
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Figure 7.2: Normalized steady-state absorption spectrum of the C$_{12}$ naphthalimide rotaxane in MeCN-d$_3$. The numbers are assigned to the peaks in Table 7.1

(1) and anti-symmetric (7) CO-stretch modes of the ni station, respectively. There is also a small contribution of the me CO-stretch vibration (8) at 1662 cm$^{-1}$. The peak at 1633 cm$^{-1}$ consists of a major contribution from the CO-stretch vibration (5) of the succ station and a minor one from the C=C-stretch mode of the aryl (10) in the ni station. This station exhibits an additional C=C-stretch peak (9) at 1605 cm$^{-1}$. All peaks in the steady-state absorption spectrum and in the spectra of the triplet and excited states of the rotaxane are summarized in Table 7.1. There are no absorption bands originating from the electron donor (DABCO) or MeCN-d$_3$ in the spectral region of interest. However, in case a sample contains traces of water, the H$_2$O bending mode can contribute to the transient absorption signal by a heating effect similar to the one described in Chap. 9.

7.2.2 UV-IR transient spectra of the rotaxane and thread

Figure 7.3 shows the UV-pump IR-probe transient absorption spectrum of the C$_{12}$ thread and rotaxane in absence of the electron donor (DABCO). After UV excitation, we observe in both samples two bleaching signals (1 and 7) associated with the symmetric and asymmetric stretch modes of the ni station, and induced absorptions of the corresponding triplet species (11 and 12). As the molecules return
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Table 7.1: Overview of the normal modes with their corresponding frequencies and description of the molecular shuttle in the ground, excited and radical anion state.

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Frequency (cm(^{-1}))</th>
<th>Hydrogen bonding</th>
<th>Type</th>
<th>Electronic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (\text{ni}_s)</td>
<td>1701</td>
<td>no</td>
<td>CO stretch</td>
<td>ground</td>
</tr>
<tr>
<td>7 (\text{ni}_{\text{as}})</td>
<td>1662</td>
<td>no</td>
<td>CO stretch</td>
<td>ground</td>
</tr>
<tr>
<td>5 succe</td>
<td>1633</td>
<td>yes</td>
<td>CO stretch</td>
<td>ground</td>
</tr>
<tr>
<td>8 mec</td>
<td>1662</td>
<td>no</td>
<td>CO stretch</td>
<td>ground</td>
</tr>
<tr>
<td>9/10 (\text{ni}^-)</td>
<td>1605/1633</td>
<td>no</td>
<td>C=C stretch (Aryl)</td>
<td>ground</td>
</tr>
<tr>
<td>11 (\text{ni}_s)</td>
<td>1632</td>
<td>no</td>
<td>CO stretch</td>
<td>triplet</td>
</tr>
<tr>
<td>12 (\text{ni}_{\text{as}})</td>
<td>1591</td>
<td>no</td>
<td>CO stretch</td>
<td>triplet</td>
</tr>
<tr>
<td>2 (\text{ni}_s^-)</td>
<td>1613</td>
<td>no</td>
<td>CO stretch</td>
<td>radical anion</td>
</tr>
<tr>
<td>3 (\text{ni}_{\text{as}}^-)</td>
<td>1592</td>
<td>yes</td>
<td>CO stretch</td>
<td>radical anion</td>
</tr>
<tr>
<td>4 succe</td>
<td>1679</td>
<td>no</td>
<td>CO stretch</td>
<td>radical anion</td>
</tr>
<tr>
<td>6 mec</td>
<td>1652</td>
<td>no</td>
<td>CO stretch</td>
<td>radical anion</td>
</tr>
<tr>
<td>13 (\text{ni}^-)</td>
<td>1531</td>
<td>no</td>
<td>C=C stretch (Aryl)</td>
<td>radical anion</td>
</tr>
<tr>
<td>14 (\text{ni}_{\text{as}}^-)</td>
<td>1564</td>
<td>no</td>
<td>CO stretch</td>
<td>radical anion</td>
</tr>
</tbody>
</table>

to the ground state, the signal decays hyperbolically \(^\dagger\) and vanishes after approximately 30 \(\mu s\).

When performing the same experiment on the \(C_{12}\) thread in the presence of DABCO (Fig. 7.4), the transient spectrum exhibits additional features. At very short delays (<100 ns), we again observe ground-state bleaching of the symmetric and asymmetric stretch modes in \(\text{ni}\) (1 and 7) and their corresponding triplet states (11 and 12). At delays longer than 100 ns, DABCO has reduced the \(\text{ni}\) station, and the triplet state evolves into the radical anion state. As a consequence, the peaks (2 and 13) of the corresponding radical anion species appear at 1613 cm\(^{-1}\) and 1564 cm\(^{-1}\). In addition, the peaks at 1633 cm\(^{-1}\) (10) and 1531 cm\(^{-1}\) (14) correspond to the bleaching and induced absorption of the aryl C=C-stretch mode in the \(\text{ni}\) station due to the radical anion formation. For longer delays, we observe an overall decay of the signal due to charge recombination.

\(^\dagger\)The charge recombination is a second-order process and hence we observe hyperbolic decay.
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Figure 7.3: Transient absorption spectra of the C\textsubscript{12} thread (A) and rotaxane (B) in absence of DABCO for several delays of the pump with respect to the probe. The labels refer to the normal modes in the Table 7.1.

Figure 7.4: Transient absorption spectra of the C\textsubscript{12} thread for short (A) and long (B) delays between the pump and probe pulses, in presence of DABCO. The labels refer to the normal modes in Table 7.1.

7.2.3 Observing molecular devices in motion

The normalized UV-IR transient spectra of the C\textsubscript{12} rotaxane at different delay times are shown in Fig. 7.5. The intensity of peak (1) depends solely on charge recombination of the radical anion. We have used this peak to normalize all transient
absorption spectra, thus eliminating the contribution of the charge recombination. As in the case of the thread, the transient spectra at early delays (from 0 to 120 ns in Fig. 7.5B) show how the triplet state of the rotaxane evolves into the radical anion state as a result of ni reduction by DABCO. After the system has been charged, i.e., after the radical anion has been formed, we can observe spectral changes reflecting the shuttling of the macrocycle from the succ to the ni$^-$ station. We can confirm this by comparing the transient absorption spectra of the rotaxane with and without DABCO (see Fig. 7.3B and 7.5C). In the latter case, we observe only the triplet state generated by the UV pulse. Since no electron donor is present, we do not observe the creation of the ni$^-$ radical anion that leads to the shuttling of the macrocycle. The peaks that change most prominently upon shuttling of the macrocycle are the positive bands at 1613 cm$^{-1}$ (2) and 1592 cm$^{-1}$ (3). These bands are assigned to the symmetric CO-stretch mode of the ni$^-$ station (ni$_{\text{suc}}$), where the latter is hydrogen-bonded to the macrocycle. The delay dependence of the intensity of these peaks can be explained by the shuttling of the macrocycle from the succ to ni$^-$ station in the following way: the shuttling of the macrocycle results in an increasing number of stronger hydrogen-bonded ni$^-$ stations, which is mirrored by the intensity of peak 3. Simultaneously, as the number of unbound ni$^-$ stations decreases, we observe the disappearance of peak 2. Complementary to this, a positive band at 1679 cm$^{-1}$ (4) and a negative band at 1633 cm$^{-1}$ (5) are observed. The former is the absorption of the non-hydrogen bonded succ CO-stretch vibration, the latter a combination of the bleaching of the hydrogen-bonded succ CO-stretch vibration and the aryl C=C-stretch vibration of the ni station. The dynamics of both peaks shows that the majority of the macrocycles leaves the succ station. The absorption observed at 1652 cm$^{-1}$ (6) is caused by hydrogen-bonding of ni$^-$ to the NH groups of the macrocycle. The macrocycle CO-stretch mode is affected by this interaction because the hydrogen-bonded NH groups are part of the same amide group as the vibrating C=O groups. The intensity of the $\Delta\alpha$ peak is low because the hydrogen-bonding interaction is removed from the oscillator by two chemical bonds. In addition, this band has some overlap with the negative peak observed at 1663 cm$^{-1}$ (7, 8). The remaining peaks at lower frequencies also undergo changes as a result of shuttling. However, they are far less pronounced than those displayed by the peaks already discussed.

To confirm our assignments, we have also compared the UV-IR spectra of the C$_{12}$ rotaxane at 120 ns and at 2000 ns with the steady-state absorption spectra of the electrochemically reduced C$_{12}$ thread and rotaxane measured by Jagesar et al. (see Fig. 7.6). In both cases, the UV-IR spectra resemble the spectra of the electrochemically reduced species very well. The fact that at short delays the UV-IR spectra are similar to the electrochemically reduced thread suggests that most of the rotaxane molecules are still at the succ station. At later delays, the macrocycle...
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Figure 7.5: A: Solvent subtracted FTIR spectrum of $10^{-4}$ M $C_{12}$ rotaxane and $10^{-2}$ M DABCO in MeCN-d$_3$, 11 mm path length. B: Transient UV-IR spectra of the $C_{12}$ rotaxane at delays ranging from 10 ns to 120 ns after UV excitation. C: Transient UV-IR spectra of the $C_{12}$ rotaxane at delays ranging from 120 ns to 2000 ns after UV excitation and molecular structures of the neutral and radical anion rotaxane. The labeled vibrations in the transient spectrum correspond with the the labeled CO groups of Fig. 7.1.
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Figure 7.6: A: Comparison of the UV-IR spectrum of the C₁₂ rotaxane at 120 ns and the spectrum of electrochemically reduced C₁₂ thread. B: Comparison of the UV-IR spectrum of the C₁₂ rotaxane at 2000 ns and the spectrum of electrochemically reduced C₁₂ rotaxane.

has shuttled and has become hydrogen-bonded to the nii⁻ station, which mirrors the situation of the electrochemically reduced rotaxane.

The peaks labeled DEPARTURE (4 and 5) and ARRIVAL (2, 3 and 6) in Fig. 7.5 correspond to the macrocycle leaving the succ station and binding to the nii⁻ station, respectively. Using time-resolved IR absorption spectroscopy we can observe the departure and arrival of the macrocycle as separate processes. The shuttling rate of the macrocycle can be obtained from the dynamics of these bands, each corresponding to a specific moiety of the rotaxane. The time evolution of the intensity of peaks 2, 3, 4, 5, and 6 is shown in Fig. 7.7. We use a least-squares double-exponential function to model the delay dependence of the five normalized transient absorption bands (the normalization removes the overall decay of the signal due to the charge recombination). The radical anion formation (k_T, dominant at early delays labeled CHARGING in Fig. 7.7) and the shuttling rate (k_s^{C₁₂}, dominant at later delays, labeled ARRIVAL and DEPARTURE in Fig. 7.7) were used as global parameters. We find k_T to be 30±5 ns⁻¹ and k_s^{C₁₂} to be 1.30±0.03 × 10⁻³ ns⁻¹ which corresponds to a shuttling lifetime (T_s^{C₁₂}) of 770±20 ns.

The observation of single-exponential dynamics in the decay of the transient absorption bands corresponding to the DEPARTURE and ARRIVAL of the macrocycle leads us to the conclusion that during the shuttling process, an individual macrocycle spends only a short amount of time on the thread compared to the
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average shuttling time of the ensemble. If a significant population of the macrocycles had resided on the carbon chain prior to creation of the \( \text{ni}^- \), one would have observed two time constants for the ARRIVAL peaks: an initial fast component originating from the macrocycles already free from the hydrogen bonds of the succ station, and a slower component for the macrocycles that still need to break these bonds. This is only true if the motion of the macrocycle along the thread is much faster than the rate at which the hydrogen bonds at the succ station are broken. In any other case, one should observe single-exponential dynamics in all bands.

7.2.4 Escape from the free-energy minimum

We will now investigate the free-energy barrier (\( \Delta G^\ddagger \)) the macrocycle has to overcome to escape from the succ station. Increasing the average thermal energy available to the macrocycle to overcome this energy barrier will result in an increase in shuttling rate. To achieve this experimentally, we measure the shuttling rate of the \( C_9 \) rotaxane at different temperatures. By increasing the temperature we increase the population of macrocycles that have enough energy to escape the succ hydrogen bonds. The shuttling rates measured for temperatures ranging from 294 K to 338 K are shown in Fig. 7.8. The data can be well described by the Eyring equa-
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Figure 7.8: $k_s^{C_9}$ Shuttling rate at different temperatures fitted with Eq. 7.1.

$$k_s(T) = \frac{k_B T}{h} e^{-\Delta G^\ddagger \over RT}$$

(7.1)

where $k_B$, $R$ and $T$ are the Boltzmann constant, the gas constant and the temperature of the system, respectively. We find that the enthalpy of activation ($\Delta H^\ddagger$) is $26.03 \pm 0.8 \text{ kJ mol}^{-1} (6.22 \pm 0.2 \text{ kcal mol}^{-1})$ and the entropy of activation ($\Delta S^\ddagger$) is $-31.7 \pm 3 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1} (-7.58 \pm 0.7 \times 10^{-3} \text{ kcal mol}^{-1} \text{K}^{-1})$. From these values we determine that $\Delta G^\ddagger_{298 \text{ K}}$ is $35.51 \pm 1.7 \text{ kJ mol}^{-1} (8.48 \pm 0.41 \text{ kcal mol}^{-1})$.

This value is in reasonable agreement with the $\Delta G^\ddagger_{298 \text{ K}}$ obtained with transient UV-VIS spectroscopy for the $C_{12}$ rotaxane: $42.7 \pm 2.9 \text{ kJ mol}^{-1} (10.2 \pm 0.7 \text{ kcal mol}^{-1})$. The value obtained for $\Delta H^\ddagger$ corresponds to 4 hydrogen bonds where the enthalpy of formation of one hydrogen bond is $-7.5 \pm 0.8 \text{ kJ mol}^{-1} \text{K}^{-1} (-1.8 \pm 0.2 \text{ kcal mol}^{-1} \text{K}^{-1})$ for N-methyl-acetamide in CDCl$_3$.

The temperature dependence of $k_s^{C_9}$ displays Arrhenius behavior. This indicates that the shuttling process is effectively a single-barrier event, and that the energy required by the macrocycle to cross the barrier is provided by thermal fluctuations. The negative activation entropy $\Delta S^\ddagger$ suggests that some ordering of the system is required before the macrocycle can escape from the succ station.
7.2.5 Rapid motion on the carbon-chain

The next step in the shuttling process is the motion of the macrocycle over the carbon-chain in the direction of either the succ station or the ni\textsuperscript{-} station. We will now explore how changing the carbon-chain length affects the probability of these events. The shuttling rates of rotaxanes with thread lengths $n = 5, 9, 12, 16$ are shown in Fig. 7.10A. We can model the data by assuming a biased random-walk mechanism for the probability $P_s(n)$ of the macrocycle ending up at the ni\textsuperscript{-} station. This probability should be proportional to the rate at which the macrocycle shuttles. The biased random-walk mechanism is equivalent to Huygens’ fifth problem, generally referred to as the Gambler’s Ruin\textsuperscript{‡}, that was first fully solved as long ago as 1733 by de Moivre.\textsuperscript{121} Assuming the probability of a motion of the macrocycle by a step of one CH\textsubscript{2} unit towards the ni\textsuperscript{-} station to be $p$, one can show that

$$k_s(n) \propto P_s(n) = \frac{1 - \left[\frac{1-p}{p}\right]}{1 - \left[\frac{1-p}{p}\right]^{(n+1)}}, \quad (7.2)$$

By fitting this model to our data we find $p = 0.44 \pm 0.01$. This means that the event of the macrocycle moving one step towards the ni\textsuperscript{-} station is slightly less probable than the event of it moving towards the succ station ($1 - p = 0.56$). In other words, there is a small bias against the macrocycle going towards the ni\textsuperscript{-} station. Nevertheless, we observe that majority of the macrocycles in the charged rotaxanes eventually resides at this station which is a consequence of its stronger hydrogen-bonding character.

We have also considered a situation in which the two consecutive steps of the macrocycle on the thread are correlated. This picture corresponds to a physical representation of a shuttling process which is depicted on Fig. 7.9. Here, we expect that first the macrocycle moves from a position 1 to a position 2 towards the ni\textsuperscript{-} station. We consider the probability of the movement of the macrocycle backwards to a position 1 or forwards to a position 3. The thread at the original position (1) is sterically more favorable for the macrocycle to reside on than at the position 3 because the thread at the this position is still close to the original geometrical conformation. We have tried to fit the data with this correlated random-walk model\textsuperscript{122} using the following equation:

$$k_s(n) \propto P_s(n) = 1 - \frac{1}{2} \left(1 + \frac{1 - \frac{2}{n+1}}{1 + \frac{\rho}{n+1}}\right), \quad \text{with} \quad \rho = \frac{2R}{1 - R}. \quad (7.3)$$

\textsuperscript{‡}The Gambler’s Ruin is a coin-flipping game in which the odds of winning or loosing are determined by the probability $p$. In case, this probability is different from 0.5 when the game is played with an unfair coin.
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![Diagram of molecular shuttle with three steps](https://via.placeholder.com/150)

**Figure 7.9:** The scheme depicts the representation of the steric barrier assumed in the correlated random-walk model of the shuttling rotaxane.

In this model, we consider a correlation \( R \) between the probabilities of each two consecutive steps of the macrocycle along the thread. In other words, the direction of the previous step (CH\(_2\) unit) of the macrocycle on the thread influences the direction of the following step. With the correlation coefficient \( R \) close to 1, two successive forward movements are very probable while if \( R \) is close to -1 such event is very unlikely. However, it is obvious from Fig. 7.10 that this model is not able to describe the experimentally observed dependence of the shuttling rate on the thread length even with \( R = -0.99 \). §

The shuttling process ends with the hydrogen-bonding of the macrocycle to the ni\(^{-}\) station, a process that occurs very fast. Due to the strong hydrogen-bond affinity of this station the probability of the macrocycle escaping from the ni\(^{-}\) station is negligible. This is confirmed by the almost complete disappearance of peak (2) representing the non-hydrogen-bonded ni\(^{-}\) station.

### 7.2.6 Shuttling mechanism

The above results show that the shuttling mechanism involves two distinct steps: the rupture of the hydrogen bonds between the macrocycle and the succe station which is driven by thermal fluctuations and described by Eq. 7.1, followed by a fast

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§The correlation \( R = 0 \) corresponds to the steepest decay of the shuttling rate as a function length of the thread.
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Figure 7.10: Thread-length \( (n) \) dependence on the shuttling rate \( k_s \) fitted with Eq. 7.2 for biased \( (p \neq 0.5) \) and unbiased \( (p = 0.5) \) random walk model, and with Eq. 7.3 for correlated random walk model \( (R = -0.99) \).

random motion of the macrocycle over the carbon-chain that ends by hydrogen-bonding to either the \textbf{succ} or \textbf{ni} \textsuperscript{-} station and described by Eq. 7.2 (see Fig. 7.10 for a pictorial representation of the mechanism). The rate of the complete shuttling process is the product of the escape rate and the probability to arrive at the \textbf{ni} \textsuperscript{-} station. We therefore obtain a formula for the shuttling rate \( k_s \) that describes the entire mechanism:

\[
k_s(T,n) \propto k_s(n) \times P_s(n) = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{R T}} \times \frac{1 - \left[1 - \frac{1-p}{p}\right]}{1 - \left[1 - \frac{1-p}{p}\right]^{(n+1)}}.
\]

(7.4)

First, all hydrogen bonds between the \textbf{mc} and \textbf{succ} \textsuperscript{3} must be broken before the macrocycle can travel over the thread. Once the macrocycle is on the thread, it has two choices: binding to the \textbf{succ} station, or to the \textbf{ni} \textsuperscript{-} station. Since the latter is thermodynamically favorable, the majority of the macrocycles will end up hydrogen-bonded to the \textbf{ni} \textsuperscript{-} station.
7.3 Conclusions

We have shown that UV-IR spectroscopy can be used to observe the motion of molecular machines with nanosecond time resolution. By probing the dynamics of the CO-stretch modes of each specific part of the molecular machine, we can investigate the elementary events of the shuttling mechanism in unprecedented detail. In particular, the departure and arrival of the shuttling macrocycle can be observed separately. Shuttling is found to occur in two steps: after escaping from the succ station (with a rate determined by Arrhenius’ law), the macrocycle resides a short time on the thread, binding almost immediately to either the ni$^-$ or succ station. We find that the motion of the macrocycle during the second step is effectively a one-dimensional biased random walk. The functioning of such molecular devices is therefore fundamentally different from macroscopic devices. Our results imply that it is impossible to predict the exact moment when an individual rotaxane will shuttle. This places a fundamental temporal limit on possible applications with this type of molecular device. If possible, tuning the bias towards a more favorable percentage would help to decrease this limit.