Chapter 4

Hetero-vibrational interactions, cooperative hydrogen bonding, and vibrational energy relaxation pathways in a rotaxane

4.1 Introduction

In the previous Chapter we have shown how 2D-IR spectroscopy allows us to determine structural information of a [2]rotaxane with sub-picosecond temporal resolution. We have focused on the interactions between the CO-stretch modes in the thread and macrocycle. However, we can also use the NH-stretch modes in the macrocycle as additional markers. Couplings between the vibrations of the NH and CO bonds (see Fig. 4.1) that are involved in the inter-component hydrogen bonds should be very sensitive to the instantaneous structure of rotaxane devices, and therefore ideally suited for studying their motions in time-resolved 2D-IR experiments. Such couplings between different types of vibrating chemical bonds can be regarded as the vibrational analogue of hetero-nuclear couplings in NMR.\(^73\) NH/CO Hetero-vibrational couplings have previously been measured in dipeptides\(^74,75\) and small organic molecules.\(^76\)

In this chapter, we show how NH/CO hetero-vibrational couplings can be used to probe the co-conformation\(^77\) of rotaxane-based devices. To this purpose, we use two-color IR pump-probe spectroscopy to study the structural and dynamical characteristics of a [2]rotaxane. In 2D-IR spectroscopy as used in the previous chapter, the pump passes through a Fabry-Perot etalon where its spectral bandwidth is decreased in order to excite one vibrational mode at the time. However, to determine
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Figure 4.1: X-ray structure of the [2]rotaxane investigated in this chapter. The insets show the angles $\theta_{\text{CO(thread)-NH}}$ and $\theta_{\text{CO(m.cycle)-NH}}$ that have been determined from the NH/CO(thread) and NH/CO(m.cycle) cross anisotropies, see section 4.3.4. In the amide group, there is an angle of $\sim 20^\circ$ between the CO-stretch transition dipole and the $C=O$ bond.62

The coupling strength, and thus the structural information, between two modes that are not within the bandwidth of the laser pulses, we have to employ two-color IR pump-probe spectroscopy generating the pump independently from the probe with a second OPA. In this way we can pump and probe any combination of modes and gain not only additional structural information, but also investigate the relaxation dynamics of the NH- and CO-stretch modes, and of the NH/CO cross peaks. Apart from the importance of vibrational relaxation in determining the energy conversion efficiency of molecular devices, knowledge of the relaxation rates and pathways is essential for the interpretation of hetero-vibrational 2D-IR spectra, since different $T_1$ lifetimes of coupled modes may give rise to apparent delay dependences of the observed couplings.

4.2 Materials and methods

Two types of experiments have been performed: one-color pump-probe experiments in which the same vibrational mode (either NH- or CO-stretch) is pumped and probed, and two-color pump-probe experiments in which the NH-stretch mode is excited and the CO-stretch modes are probed. The setups employed in the one-color and two-color experiments are described in Sections 2.3.3 and 2.3.5, respectively.

All experiments were carried out at room temperature on 2.5 mM solution of
the [2]rotaxane in CDCl$_3$. To remove traces of water from the CDCl$_3$, it is distilled at atmospheric pressure, and the rotaxane solution is prepared under Ar atmosphere. The sample is kept in a sealed cell consisting of two CaF$_2$ windows separated by a 1 mm spacer. We observe a non-resonant response (mainly from the solvent) at delays where the pump and probe pulse are temporally overlapped. To ensure that these non-resonant effects do not influence the quantitative interpretation, all data analysis is done starting from delay values (400 fs for the NH-pump/NH-probe, 700 fs for the other experiments) at which the non-resonant contribution has become negligible compared to the resonant signal. In some of the measurements, a small thermal contribution to the signal is observed at long pump-probe delays. This thermal signal is due to a small increase in the temperature of the sample after vibrational relaxation (at most 0.1 K, as estimated from the focal diameter and pulse energy). In the least-squares fitting of the data, this thermal contribution is assumed to grow in with the rate of the vibrational relaxation.

4.3 Results and discussion

4.3.1 General considerations

Figure 4.2 shows the steady-state absorption spectrum of the [2]rotaxane in CDCl$_3$. The peaks at 1610 cm$^{-1}$ and 1660 cm$^{-1}$ are due to the CO-stretch modes of the thread and the amide I mode of the macrocycle, respectively. The peak at 3370 cm$^{-1}$ is due to the amide A mode of the macrocycle (the thread does not contain any NH groups). As the amide I mode involves mainly the stretching of the CO bond, and the amide A mode mainly that of the NH bond, in the following these modes will simply be referred to as CO-stretch and NH-stretch mode, respectively. Because of the symmetry of the rotaxane, the two CO groups in the thread are equivalent, and the same holds for the four CO groups and four NH groups in the macrocycle. The amplitude of the peaks of the CO-stretch modes is much larger than that of the NH-stretch modes, but the frequency-integrated absorption cross sections are comparable, since the FWHM of the NH-stretch band is larger by approximately the same factor. In all experiments, spectral diffusion is not observable because the power spectrum of the excitation pulse is broader than the widths of the absorption bands that are resonantly excited.

4.3.2 NH-stretch mode

The linear and the transient absorption spectra for parallel and perpendicular polarizations of the pump and probe beams are shown in Figure 4.3a. From the ratio of the parallel and perpendicular signals, we find an anisotropy of 0.36, close to
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Figure 4.2: Infrared absorption spectrum of a 2.5 mM solution of the investigated [2]rotaxane in CDCl₃. The colors of the peaks match those of the highlighted bonds in the chemical structure. The dotted curve represents the NH-stretch absorption multiplied by a factor of 10.

the theoretically expected value of 0.4. From the transient spectra, we can determine the diagonal anharmonicity (difference between the \( v = 0 \rightarrow 1 \) and \( v = 1 \rightarrow 2 \) transition frequencies) of the NH-stretch mode. Since the power spectrum of the excitation pulse is much broader than the NH-stretch absorption band \( \alpha_0(\nu) \), the entire absorption band is excited simultaneously. As a consequence, spectral diffusion is not observable, and the absorption change due to ground-state bleaching and stimulated emission can be well described by a negative contribution with the shape of the steady-state absorption spectrum \( \alpha_0(\nu) \). We assume that the \( v = 1 \rightarrow 2 \) line shape is similar to the \( v = 0 \rightarrow 1 \) line shape, but allow for a difference in width (to account for faster dephasing of the \( v = 1 \rightarrow 2 \) transition as compared to the \( v = 0 \rightarrow 1 \) transition, for instance as a consequence of faster vibrational relaxation of the \( v = 2 \) state), and an intensity scaling factor (to allow a deviation from the harmonic approximation, in which this scaling factor would be unity\(^5\)). Using a Gaussian to describe \( \alpha_0(\nu) \), this simple approach provides a good description of the observed \( \Delta \alpha(\nu) \) (see Fig. 4.3a). From a least-squares fit to the data at 1 ps delay we obtain a value of \( 153 \pm 4 \text{ cm}^{-1} \) for the NH-stretch anharmonicity, similar to the values reported elsewhere for the diagonal anharmonicities of the NH-stretch (amide A) mode of amide groups in peptides.\(^7\)^\(^4\),\(^7\)^\(^9\)

Figure 4.3b shows the transient absorption change as a function of delay between the pump and probe pulses for several probing frequencies. We find that the
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Figure 4.3: (a) Linear and transient absorption spectra for parallel and perpendicular polarization of the probe with respect to the pump. The solid lines are least-squares fits using a Gaussian function to describe the absorption band. (b) Transient absorption change of the NH-stretch mode as a function of delay between pump and probe pulse for several representative probing frequencies. The solid lines are least-squares fits to single-exponential decays.

delay dependence can be well described by a single-exponential decay, and from a simultaneous least-square fit to the delay-dependent absorption changes at all probing frequencies (using the same time constant for all frequencies) we find an excited-state lifetime $T_1$ of 2.24 ± 0.12 ps. The observed lifetime is significantly longer than the 0.58 ps observed for the dipeptide acetyl-proline-OMe in chloroform. In chloroform, acetyl-proline-OMe is in the $C_7$ conformation, which contains an internal NH···OC hydrogen bond, leading to a redshifted NH-stretch frequency of 3333 cm$^{-1}$. This NH-stretch frequency is lower than that of the rotaxane (3370 cm$^{-1}$), which implies that the hydrogen bonding in the dipeptide is stronger than in the rotaxane. The stronger hydrogen bonding probably explains the faster vibrational relaxation in the peptide as compared to the rotaxane.

4.3.3 CO-stretch modes

Figure 4.4 shows the transient absorption change upon exciting the CO-stretch region (the spectrum of the pump pulse covers both the thread and macrocycle CO-stretch modes). The spectrum can be quantitatively analyzed in the same way as the NH-stretch mode: the absorption bands of the thread and macrocycle CO-stretching modes are each modeled by a Gaussian, and the transient-absorption spectrum of each mode as the sum of a bleaching/stimulated-emission part identical
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to the absorption band and a redshifted induced absorption which is modeled as a Gaussian. From a least-squares fit we find diagonal anharmonicities of $10\pm3$ cm$^{-1}$ and $5\pm3$ cm$^{-1}$ for the thread and macrocycle CO-stretch modes, respectively, in agreement with the estimate from the 2D-IR spectrum (see Chapter 3). To investigate if energy transfer between the CO-stretch modes occurs, we have also performed experiments in which either the thread or the macrocycle CO-stretch mode is selectively pumped with a narrow-band pump pulse (FWHM 13 cm$^{-1}$), and both modes are probed. We then observe decays with the respective $T_1$’s at the thread or macrocycle mode, but no energy transfer between the modes.

![Figure 4.4](image_url)

**Figure 4.4:** Linear (blue points) and transient-absorption spectrum at a delay of 1 ps (red points) showing the frequency region containing the CO-stretch modes of the thread (1610 cm$^{-1}$) and the macrocycle (1655 cm$^{-1}$). The solid lines are the result of least-squares fits assuming Gaussians for the lineshapes.

The delay dependence of the absorption change is shown in Figures 4.5(a) and 4.5(b). From simultaneous least-squares fits of exponential decays for the CO-stretch modes of the thread and of the macrocycle we find $T_1$ values of $0.79\pm0.12$ ps and $0.96\pm0.07$ ps, respectively.
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Figure 4.5: (a) Transient absorption change of the thread CO-stretch mode as a function of delay between pump and probe pulse for several representative probing frequencies. The solid lines are simultaneous least-square fits of a single-exponential decay. (b) The same as (a), for the CO-stretch mode of the macrocycle.

4.3.4 NH-CO interactions

Cross anharmonicities

The response of the CO-stretch modes upon excitation of the NH-stretch mode is shown in Figure 4.6, together with the NH-stretch response. This graph can be regarded as a cross section through a two-dimensional IR spectrum, where the NH-response is the diagonal peak and the positive-negative doublets in the CO-stretch region are cross-peaks. For both CO-stretch modes, the signal rises instantaneously (within the system response of ∼250 fs). This implies that no energy transfer from the NH-stretch to either of the CO-stretch modes takes place, since such energy transfer would imply an ingrowth of the CO-stretch signal with a time constant equal to the ∼2.2 ps lifetime of the NH-stretch mode. Hence, the NH-CO cross peaks must be due to coupling between the NH- and CO-stretch modes. From the shape and amplitude of each of the two CO-stretch cross peaks the corresponding cross-anharmonicity (the difference between the frequency of the \( |v_{\text{NH}} = 1, v_{\text{CO}} = 0 \rangle \rightarrow |v_{\text{NH}} = 1, v_{\text{CO}} = 1 \rangle \) and \( |v_{\text{NH}} = 0, v_{\text{CO}} = 0 \rangle \rightarrow |v_{\text{NH}} = 0, v_{\text{CO}} = 1 \rangle \) transitions) can be determined, as well as the cross-peak anisotropy (dependence on the relative polarization of pump and probe). The shape of each cross-peak can be described as the sum of a negative part caused by the bleaching of the common vibrational ground state upon excitation of the NH-stretch mode, and a positive part due to the induced absorption from the \( |v_{\text{NH}} = 1, v_{\text{CO}} = 0 \rangle \) to the \( |v_{\text{NH}} = 1, v_{\text{CO}} = 1 \rangle \) state (which occurs at a frequency lower than the fundamental \( |v_{\text{NH}} = 0, v_{\text{CO}} = 0 \rangle \) frequency).
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\[0 \rightarrow |v_{NH} = 0, v_{CO} = 1\rangle\) transition:

\[
\Delta \alpha_{\text{cross}}(v) = -\alpha_0(v) + \alpha_0(v + \Delta_{\text{CO-NH}}),
\]

(4.1)

where it is assumed that the CO-stretch lineshape \(\alpha_0(v)\) does not change upon excitation of the NH-stretch mode. We model each of the two cross peaks (for the macrocycle and thread CO-stretch modes) by the above expression, using Gaussians for \(\alpha_{0,\text{thread}}(v)\) and \(\alpha_{0,\text{m.cyc}}(v)\), which we obtain from a least-squares fit to the steady-state absorption spectrum. Fitting this model to the CO-stretch transient spectrum, treating the two cross-anharmonicities \(\Delta_{\text{CO(thread)-NH}}\) and \(\Delta_{\text{CO(m.cyc)-NH}}\) and the cross-peak anisotropies as free parameters, we obtain the fit shown as the solid curves in Fig. 4.6. From this fit, we obtain \(\Delta_{\text{CO(thread)-NH}} = 9.5 \pm 2.2 \text{ cm}^{-1}\) and \(\Delta_{\text{CO(m.cyc)-NH}} = 5.1 \pm 2.4 \text{ cm}^{-1}\) for the cross anharmonicities, and \(R_{\text{CO(thread)-NH}} = 0.15\) and \(R_{\text{CO(m.cyc)-NH}} = 0.22\).

![Figure 4.6](image)

**Figure 4.6:** Linear (blue points) and transient absorption change (red and black points) upon exciting the NH-stretch mode. The solid black and red lines show the pump-probe spectrum at 1 ps delay for parallel and perpendicular polarization, respectively.

The cross anharmonicity between the NH-stretch and CO\(_{\text{m.cyc}}\)-stretch mode is essentially a property of the amide group, and should therefore be comparable to the cross anharmonicity observed between the NH-stretch (amide A) and CO-stretch (amide I) modes of the amide group in acetyl-proline-OMe in chloroform. For the latter, a value of \(3.5 \pm 0.3 \text{ cm}^{-1}\) is observed,\(^{74}\) which agrees well with the \(5.1 \pm 2.4 \text{ cm}^{-1}\) observed here.
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The $\Delta_{\text{CO(thread)-NH}}$ cross anharmonicity arises from interaction between the macrocycle-NH and thread-CO groups across the hydrogen-bond connecting them. Although this interaction is very sensitive to the strength and direction of the NH···OC hydrogen bond, a quantitative interpretation of the observed cross anharmonicity in terms of specific conformational parameters requires detailed quantum-chemical modeling of the influence of hydrogen bonding on the cross anharmonicity. At present, such models are not yet available, although theoretical work in this direction is actively being pursued.$^{81, 82}$

It is interesting to compare the value of $9.5 \pm 2.2$ cm$^{-1}$ observed for the NH/CO$_{\text{thread}}$ cross-anharmonicity to that between the hydrogen-bonded NH and CO groups in the peptide acetyl-proline-OMe. In chloroform this peptide adopts the C$_7$ conformation, and contains an internal NH···OC hydrogen bond.$^{74}$ Both in the peptide and in the rotaxane, the NH/CO cross-anharmonicity arises mainly from through-hydrogen bond effects. In the peptide, the NH-stretch frequency is lower than in the rotaxane (3333 cm$^{-1}$ vs. 3370 cm$^{-1}$), which implies that the NH···OC hydrogen bond is stronger in the peptide than in the rotaxane.$^{83}$ One would therefore expect a stronger NH/CO anharmonic interaction in the peptide, and hence a higher NH/CO cross anharmonicity. Surprisingly, the exact opposite is observed: the cross-anharmonicity of the CO and NH groups connected by the hydrogen bond is much smaller in the peptide than in the rotaxane (1.4 ± 0.4 cm$^{-1}$ in the peptide,$^{74}$ $9.5 \pm 2.2$ cm$^{-1}$ in the rotaxane). We believe that the stronger

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**Figure 4.7:** (a) Delay dependence of the thread CO-stretch response at 1599 cm$^{-1}$ (red points) and 1613 cm$^{-1}$ (blue points), and of the NH-stretch response at 3242 cm$^{-1}$ (gray points). The probing frequencies are indicated by arrows in the inset. (b) Delay dependence of the CO-stretch response of the macrocycle at 1640 cm$^{-1}$ (red points) and 1665 cm$^{-1}$ (blue points), and of the NH-stretch response at 3242 cm$^{-1}$ (gray points). The green curve shows a single-exponential fit to the CO-stretch data, the red and blue curves are double-exponential fits.
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Anharmonic interaction between the NH- and CO-stretch modes observed in the rotaxane is due to a cooperativity effect\textsuperscript{83,84} of the two NH···OC hydrogen bonds coordinated to the same CO group (see Figure 4.1). Each NH···OC hydrogen bond polarizes the charges of the CO group in such a way as to enhance the anharmonic NH/CO interaction through the other NH···OC hydrogen bond. Hence, even though the individual hydrogen bonds are weaker in the rotaxane than in the peptide, the cooperative effect of a double hydrogen bond to the same acceptor leads to an amplification of the anharmonic NH/CO interaction, giving rise to the larger NH/CO cross anharmonicity in the rotaxane.

Cross anisotropies and structural information

The cross-peak anisotropies $R_{ij}$ are directly related to the angle $\theta_{ij}$ between the transition-dipole moments of the coupled vibrations:\textsuperscript{51}

$$R_{ij} = (3 \cos^2 \theta_{ij} - 1)/5. \quad (4.2)$$

Using this expression we obtain angles $\theta_{\text{CO(thread)-NH}} = 139^\circ$ and $\theta_{\text{CO(m.cycle)-NH}} = 33^\circ$ (see Fig. 4.1 for the definition of the angles). The angle of $33^\circ$ between the NH- and CO-stretch mode transition dipoles of the amide group of the macrocycle is very similar to the value of $34.5 \pm 3^\circ$ found for this angle in the amide group of acetyl-proline-OMe,\textsuperscript{74} a peptide in which the amide group forms an internal NH···OC hydrogen bond (in non-hydrogen-bonded peptides, a smaller value of $23 \pm 3^\circ$ is found\textsuperscript{75}). The similarity of the dipole-dipole angles in the rotaxane and in the hydrogen-bond containing peptide suggests that the value of this angle is determined mainly by the presence (and strength) of a hydrogen bond, independent of whether the amide group is in a peptide or in a rotaxane. Assuming an angle of $20^\circ$ between the amide I transition dipole and the C=O bond,\textsuperscript{62} we obtain an angle $\angle(\text{N}^{}-\text{H}, \text{C}=\text{O}_\text{m.cycle})$ of $\sim 15^\circ$, close to the value of $12^\circ$ in the X-ray structure.\textsuperscript{4,85}

The angle between the NH-stretch mode of the macrocycle and the CO-stretch mode of the thread is directly related to the relative position and orientation of the two rotaxane components. Assuming that the CO-stretch transition dipole is parallel to the C=O bond, and the NH-stretch transition dipole parallel to the N–H bond,\textsuperscript{62} we predict an angle $\angle(\text{N}^{}-\text{H}, \text{C}=\text{O}_\text{thread})$ (indicated in Figure 4.1) of $139^\circ$ from the observed cross-peak anisotropy. This value again agrees well with the angle in the X-ray structure,\textsuperscript{4} which is $\angle(\text{N}^{}-\text{H}, \text{C}=\text{O}_\text{thread}) = 114^\circ.\textsuperscript{85}$ The discrepancy may be due to a difference between the solution and X-ray structures, but could also be due to a small angle between the thread C=O bond and the CO-stretch transition-dipole moment. It may be noted that although both the cross anharmonicity and the cross anisotropy are sensitive probes of the rotaxane co-conformation, unlike the
cross-anharmonicity, the cross anisotropy can be used in a straightforward manner to obtain quantitative information (notably the angles indicated in Figure 4.1) about the relative orientation of the macrocycle and the thread.

**NH-CO cross-peak dynamics**

We have studied the cross-peak relaxation dynamics in the rotaxane by measuring two-color pump-probe spectra as a function of delay. In these experiments, the NH-stretch mode is excited and the dynamics of the CO-stretch modes is probed. The result for the CO\textsubscript{thread}-stretch mode of the thread is shown in Fig. 4.7(a). From a least-squares fit (solid lines in Fig. 4.7(a)), we find that the decay of the CO\textsubscript{thread}-stretch response occurs with a time constant of $2.36 \pm 0.15$ ps (and a very small component with a time constant of $18 \pm 4$ ps). This decay exactly matches that of the $v = 1$ population of the NH-stretch mode ($T_1 = 2.24 \pm 0.12$ ps), as can be seen from the grey curve which represents the decay of the NH-stretch excited state absorption. Together with the instantaneous ingrowth of the CO-stretch signal, this implies that the NH-CO\textsubscript{thread} cross peak is caused purely by a coupling between the NH-stretch mode and the CO\textsubscript{thread}-stretch mode, and involves no other modes: the cross peak vanishes together with the $v = 1$ population of the NH-stretch mode.

Interestingly, in case of the macrocycle CO-stretch mode, the decay of the cross-peak intensity is much slower than that of the NH-stretch excited-state population, see Figure 4.7(b). From a simultaneous bi-exponential least-squares fit we find decay constants of $2.4 \pm 0.2$ and $7.2 \pm 0.12$ ps, respectively, with comparable amplitudes for the two components. The data cannot be described by a single-exponential decay (green curve in Fig. 4.7(b)). Apparently, the CO-stretch mode of the macrocycle is coupled not only to the NH-stretch mode, but also to another mode, which we will refer to as X. Since a coupling between the macrocycle CO-stretch mode and mode X is observed after excitation of the NH-stretch mode, we can conclude that mode X acts as an accepting mode in the energy relaxation of the NH-stretch mode. A similar phenomenon has been reported and interpreted previously by Rubtsov \textit{et al.} and we use their model (shown schematically in Figure 4.8) to describe our data. The relaxation of the NH-stretch mode involves a transfer of the vibrational energy to mode X, which acts as an intermediate state in the vibrational relaxation process. The excited state of mode X is thus populated with a time constant equal to the $T_1$ of the NH-stretch mode, and it subsequently relaxes with a time constant $\tau$. The CO\textsubscript{m,cycle}-stretch mode is coupled to both the NH-stretch mode and to mode X, and hence the delay dependence of the cross-peak intensity is governed by both time constants $T_1$ and $\tau$. In the kinetic model of Rubtsov \textit{et al.}, the excited-state populations of the NH-stretch mode and mode X
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![Diagram]

**Figure 4.8:** Left: energy level diagram illustrating the effect of the vibrational relaxation of the NH-stretch mode on the CO-stretch mode of the macrocycle ring. Right: delay dependence of the NH-CO\textsubscript{m,cycle} cross peak intensity (red points), and a least-squares fit of Eq. 4.5 to the data (red curve). The excited-state populations of the NH-stretch mode and the accepting mode X are shown as the gray and green curves.

The NH-CO\textsubscript{m,cycle} cross-peak can be easily shown to be given by

\[ n_{10}(t) = e^{-t/T_1} \] (4.3)

\[ n_{00X}(t) = \frac{T_1^{-1}}{T_1^{-1} - \tau^{-1}} (e^{-t/\tau} - e^{-t/T_1}) \] (4.4)

where the labeling of the states is as in Fig. 4.8. The NH-CO\textsubscript{m,cycle} cross-peak is due to two contributions: (i) a coupling between the CO\textsubscript{m,cycle}-stretch and the NH-stretch mode, and (ii) a coupling between the CO\textsubscript{m,cycle}-stretch and the accepting mode X. The delay-dependent cross-peak intensity is then given by

\[ I_{NH-CO}(t) = \Delta_{NH-CO} \cdot n_{10}(t) + \Delta_{X-CO} \cdot n_{00X}(t), \] (4.5)

where \( \Delta_{NH-CO} \) is the NH-CO cross-anharmonicity, and \( \Delta_{X-CO} \) the X-CO cross anharmonicity. Fitting this expression to the observed decay of the cross-peak intensity (with the ratio \( \Delta_{X-CO}/\Delta_{NH-CO} \) and an overall scaling factor as the free parameters) we obtain \( \Delta_{X-CO}/\Delta_{NH-CO} = 0.40 \pm 0.01 \), which implies that the CO-stretch mode interacts more strongly with the NH-stretch mode than with the accepting mode X. The result of the fit, and the corresponding populations \( n_{10}(t) \) and \( n_{00X}(t) \) are shown in Fig. 4.8. From this graph, it can be seen that at short pump-probe delays, the cross-peak intensity represents mainly the coupling between the CO and the NH modes, whereas at delays beyond \( \sim 4 \) ps it represents mainly the coupling between the CO and the X mode. This result clearly illustrates the importance of detailed knowledge of the relaxation dynamics for the interpretation of hetero-vibrational 2D-IR spectra.
4.4 Conclusions

In this chapter, we have shown that hetero-vibrational pump-probe IR spectroscopy is a suitable experimental technique to probe the co-conformation of a rotaxane. By calculating the NH/CO cross-peak anisotropies it allows to directly calculate the angles between the NH and CO groups in the macrocycle and thread, indicated in Figure 4.1. The cross anharmonicities are found to exhibit a similar sensitivity to the rotaxane co-conformation, and to reflect the cooperativity of the macrocycle–thread hydrogen bonding. By monitoring the appearance and disappearance of specific NH/CO cross peaks, the hydrogen-bond making and breaking at specific hydrogen-bonding sites of a molecular device can be observed separately and with sub-picosecond temporal resolution.