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Two-Dimensional Vibrational Spectroscopy of Rotaxane-Based Molecular Machines

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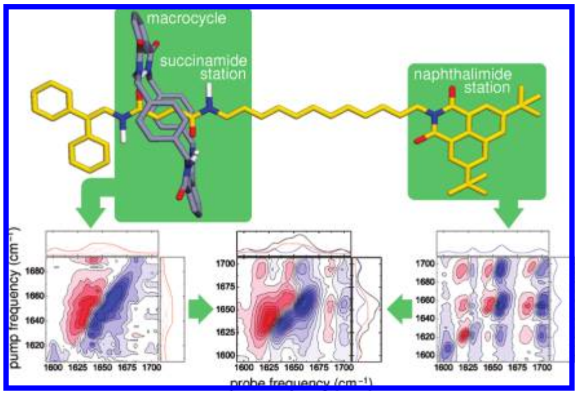

It has recently become possible to synthesize mechanical devices the size of a single molecule. Although it is tempting to regard such molecular machines as nanoscale versions of their macroscopic analogs, many notions from macroscopic mechanics no longer apply at a molecular level. For instance, the concept of viscous friction is meaningless for a molecular machine because the size of the solvent molecules that cause the friction is comparable to that of the machine itself. Furthermore, in many cases, the interactions between a molecular machine and its surroundings are comparable to the force driving the machine. As a result, a certain amount of intrinsic randomness exists in the motion of molecular machines, and the details of their mechanics are largely unknown.

For a detailed understanding of the mechanical behavior of molecular machines, experiments that probe their motion on an ultrafast time scale, such as two-dimensional (2D) vibrational spectroscopy, are essential. This method uses coupling between vibrational modes in a molecule to investigate the molecular conformation. The coupling shows up as off-diagonal peaks in a 2D graph of the vibrational response of the molecule, analogous to the spin coupling observed in multidimensional NMR spectroscopy. Both spin coupling and vibrational coupling are sensitive probes of the molecular conformation, but 2D vibrational spectroscopy shows orders of magnitude better time resolution than NMR.

In this Account, we use 2D vibrational spectroscopy to study molecular machines based on rotaxanes. These devices consist of a linear thread and a macrocycle that is noncovalently locked onto the thread. In the rotaxanes we study, the macrocycle and the thread both contain CO and NH groups. By determining the coupling between the stretching modes of these goups from the cross peaks in the 2D spectrum, we directly and quantitatively probe the relative position and orientation of the macrocycle and the thread for both a small model rotaxane and a rotaxane-based molecular shuttle.

Our results demonstrate the feasibility of using time-resolved 2D-IR experiments to measure externally triggered structural changes of molecular devices with subpicosecond time resolution. We can observe each of the elementary events that underlie the mechanical motion separately. With this ability to investigate the nature of the mechanical motions at the molecular level and with unprecedented time resolution, we expect that 2D-IR spectroscopy on molecular machines will lead to new insights into their function.

Introduction

To investigate the dynamical behavior of molecular machines[1−3] requires time-resolved methods with high structural sensitivity. Ideally, one would like to be able to determine the relative positions and orientations of the components of the machine. This kind of structural sensitivity can be accomplished using two-dimensional infrared spectroscopy.

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With 2D-IR spectroscopy, molecular conformations are determined by measuring couplings between molecular vibrations. The method was inspired by multidimensional NMR spectroscopy, in which couplings between nuclear spins are used for structure resolution.[4] Like nuclear spins, vibrations that involve stretching of specific chemical bonds are well localized in the molecule. The coupling between vibrations depends strongly 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.[5−10] The important advantage of 2D-IR spectroscopy compared with multidimensional NMR spectroscopy is its time resolution: the conformation can be determined with a time resolution determined by the duration of the optical pulses, which can be as short as 100 fs. As a consequence, it should be possible to use 2D-IR spectroscopy to study motion in molecular systems on a time scale comparable to that of the elementary molecular motions. To this purpose, one would externally trigger the motion and monitor the subsequent structural changes by recording 2D-IR spectra at different time delays with respect to the trigger. In this way, it becomes possible to construct a "movie" of the molecular motion.[11−13]

A first step toward such time-resolved 2D-IR experiments on rotaxane-based devices is to investigate how the relative positions and orientations of the mechanically interlocked components of these devices can be determined from their 2D-IR spectra. Here we give a brief overview of these investigations, including recent developments. We first demonstrate how the co-conformation (the relative position and orientation of constituent components of a supramolecular system) of a short model rotaxane can be determined from different types of 2D-IR spectra. This model rotaxane contains a structural motif also present in a number of rotaxane-based molecular machines. In the second part, we show that in an actual molecular machine, the spectral congestion may require special strategies to interpret the 2D-IR spectra but that structural information can still be obtained.

Probing the Co-conformation of a Rotaxane

Our initial experiments focused on the rotaxane shown in Figure 1A, which is composed of a benzylic amide macrocycle mechanically interlocked onto a succinamide-based thread and held in position by a network of hydrogen bonds.[14] The same structural motif recurs in the molecular shuttle discussed in the second half of this Account. Figure 1B shows the conventional infrared absorption spectrum of this rotaxane in $CHCl_3$. The peaks at 1610 and 1660 cm^{-1} are due to the CO-stretching modes of the thread and the macrocycle, respectively. Due to the symmetry of the rotaxane, the four C═O groups in the macrocycle are equivalent, and the same holds for the two CO groups in the thread. The coupling between the CO-stretching modes within the ring and thread is so small compared with the line widths that the vibrational excitations are localized on single CO bonds.[15]

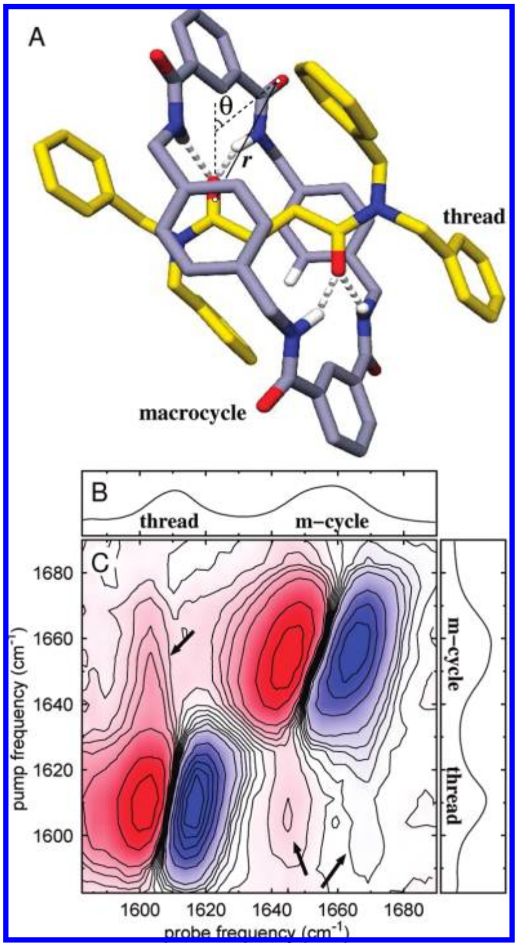

FIGURE 1. (A) Short rotaxane, the structure of which also occurs in rotaxane-based molecular shuttle of Figure 3. The carbon atoms in the thread are colored yellow, and only hydrogen atoms involved in hydrogen bonds are shown. The distance r and angle θ that have been determined from the 2D-IR spectrum are indicated. (B) Absorption spectrum of the rotaxane in the CO-stretching region. (C) 2D-IR spectrum of the rotaxane. Blue indicates negative absorption change; red indicates positive absorption change. Arrows indicate the cross peaks due to coupling between the CO-stretching modes of the thread and macrocycle.

Figure 1C shows the two-dimensional vibrational spectrum of this rotaxane, recorded in a double-resonance experiment.[15] In this experiment, a narrow-band (10 cm^{-1} fwhm) pump pulse excites the sample at a specific frequency ν_{pump}, and the resulting absorption change is determined for a range of probe frequencies ν_{probe}. Plotting the absorption change as a function of (ν_{probe},ν_{pump}), one obtains the 2D-IR spectrum. At the diagonal of the 2D graph, two intense positive−negative doublets are observed that arise from resonant excitation of the CO-stretching modes of the macrocycle and the thread. Transfer of population from the $v = 0$ to the $v = 1$ state leads to a negative absorption change at the $v = 0 \rightarrow 1$ transition frequency (caused by bleaching and $v = 1 \rightarrow 0$ stimulated emission), and a positive absorption change at the $v = 1 \rightarrow 2$ transition frequency. Since the anharmonic shift Δ (the shift of the $v = 1 \rightarrow 2$ frequency with respect to the $v = 0 \rightarrow 1$ frequency) is comparable to the homogeneous linewidths of the CO-stretching modes, the positive and negative absorption changes overlap. The negative extrema along the probe axis therefore occur at frequencies slightly higher than the $v = 0 \rightarrow 1$ transition frequencies.

From the shape of the contours on the diagonal, it is clear that the spectral response of the thread and macrocycle CO-stretching bands depends on the pump frequency: for low pump frequency, the positive and negative extrema occur at lower probing frequencies than for high pump frequency. This implies that the CO-stretching bands are inhomogeneously broadened: there exists a distribution of CO-stretching frequencies, which is static on the 1 ps time scale of the experiment. The stretching frequency of a C═O group involved in a hydrogen bond depends on the length of this hydrogen bond,[16] and the spectral inhomogeneity of the CO bands therefore most likely arises from a distribution of CO···HN hydrogen-bond lengths. The width of the inhomogeneous distribution can be derived from the slope of the contours.[17]

In the off-diagonal regions of the 2D-IR spectrum cross peaks are observed, the most prominent of which have been indicated by arrows in Figure 1C. The presence of these cross peaks arises from coupling between the CO-stretching modes of the macrocycle and those of the thread. Like the diagonal peaks, each cross peak consists of a positive−negative doublet (most clearly seen for the cross peak at the right bottom). This positive−negative doublet structure is a general characteristic of cross peaks and can be understood as follows. When there is a coupling between two modes a and b, the frequency of the state in which both modes are in the $v = 1$ state is lower than $\nu_a + \nu_b$ by the cross-anharmonicity x_{ab}.[5] As a consequence, exciting one of the modes effectively gives rise to a change of $-x_{ab}$ in the frequency of the other. This frequency change is in general smaller than the line width, so the difference in absorption between the original and the shifted peak looks approximately like the derivative of the absorption peak, and the height of the cross-peak is proportional to the coupling between the modes.[5] For the cross peak at the bottom right, the positive−negative feature is clearly observed. The cross peak in the left-top part of the 2D plot overlaps with the much stronger $v = 1 \rightarrow 2$ excited-state absorption of the macrocycle CO stretching mode on the diagonal, and the negative part of the cross peak around $(\nu_{\text{probe}}, \nu_{\text{pump}}) = (1620, 1660)$ cm^{-1} is superimposed on the much bigger positive contribution from the diagonal peak.

Obtaining Structural Parameters from the Cross Peaks

The cross-peak intensity is a direct measure of the coupling β between the thread and macrocycle CO-stretch modes, but it also depends on the relative polarizations of the pump and probe pulses. In the case that the coupled transition dipoles (C═O groups) are parallel, the cross-peak intensity for parallel pump−probe polarizations is 3 times larger than that for perpendicular pump−probe polarizations ($I_{\parallel}/I_{\perp} = 3$). In the case that the transition dipoles are not parallel, this intensity ratio is smaller. For two coupled modes a and b, the cross-peak intensity ratio $I_{\parallel}/I_{\perp}$ is related directly to the angle θ_{ab} between their transition dipoles:[5]

$$R_{ab} \equiv \frac{I_{\parallel}/I_{\perp} - 1}{I_{\parallel}/I_{\perp} + 2} = \frac{3\cos^2\theta_{ab} - 1}{5} \qquad (1)$$

where R_{ab} is the so-called cross-peak anisotropy. From the combined information of the cross-peak intensity and anisotropy, one can determine the magnitude of the coupling β between the CO-stretch modes and the angle θ between their transition-dipole moments (see Figure 1A). From a detailed quantitative analysis of the 2D data (taking into account the spectral inhomogeneity and using the full Hamiltonian of the system),[15] we obtain $\beta = -3.3 \pm 0.7$ cm^{-1} and $\theta = 48° \pm 10°$.

The angle θ is a conformational parameter that tells us directly the orientation of the macrocycle with respect to the thread (see Figure 1A). Using this angle, we can now also determine the distance r between the macrocycle and thread carbonyl groups from the macrocycle−thread coupling β. In the dipole−dipole approximation for the coupling strength, the coupling between two vibrational modes a and b is given by[18]

$$\beta = \frac{1}{4\pi\varepsilon_0}\left[\frac{\vec{\mu}_a \cdot \vec{\mu}_b}{r^3} - 3\frac{(\vec{r} \cdot \vec{\mu}_a)(\vec{r} \cdot \vec{\mu}_b)}{r^5}\right] \qquad (2)$$

where $\vec{\mu}_i$ are the transition dipoles, and $\vec{r}$ is the distance vector between the two transition dipoles. The magnitude of this coupling is thus determined by both the angle and the distance between the coupled C═O groups in the macrocycle and thread.[5] Using the known magnitudes of the transition dipole moments (obtained from the integrated absorption spectrum) and the experimentally determined angle θ between the transition dipole moments, we can determine the distance r (see Figure 1A) as $r = 6.9 \pm 0.9$ Å. Both structural parameters r and θ are in reasonable agreement with the values in the crystal structure, 59° and 5.1 Å. The discrepancy may represent a slight difference between the coconformations in solution and in the crystalline phase (packing effects), but it may also be due to the approximations used in our modeling of the data (in particular the dipolar approximation of eq 2, which at short distance overestimates the coupling).

"Heterovibrational" Couplings As a Probe of Intercomponent Geometry

The mechanical stability of devices based on rotaxanes of the type shown in Figure 1a involves NH···OC hydrogen bonds between the constituent components.[19] When there is more than one hydrogen-bonding site, externally induced changes in the hydrogen-bond affinities can be used to move the components with respect to each other in a controlled way, an effect that has been used to construct rotaxane-based molecular shuttles (see the next section).[20] Couplings between the vibrations of the NH and CO bonds that are involved in the intercomponent hydrogen bonds should be very sensitive to the co-conformation 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 analog of heteronuclear couplings in NMR.[4]

Figure 2 shows how NH/CO heterovibrational couplings can be used to probe the co-conformation of rotaxane-based devices. The response of the CO-stretch modes upon excitation of the NH-stretch mode is shown in Figure 2B, together with the NH- and CO-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. The observed NH−CO cross peaks are 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 $|v_{\mathrm{NH}} = 1, v_{\mathrm{CO}} = 0\rangle \rightarrow |v_{\mathrm{NH}} = 1, v_{\mathrm{CO}} = 1\rangle$ and $|v_{\mathrm{NH}} = 0, v_{\mathrm{CO}} = 0\rangle \rightarrow |v_{\mathrm{NH}} = 0, v_{\mathrm{CO}} = 1\rangle$ transitions) can be determined,[5] as well as the cross-peak anisotropy (see previous section).

For the two cross anharmonicities, we find $\Delta_{\mathrm{CO(thread)-NH}} = 9.5 \pm 2.2$ cm^{-1} and $\Delta_{\mathrm{CO(macrocycle)-NH}} = 5.1 \pm 2.4$ cm^{-1}. The cross anharmonicity between the NH-stretch and CO$_{\mathrm{macrocycle}}$-stretch mode is essentially a property of the amide group, and is comparable to the cross-anharmonicity observed between the NH-stretch and CO-stretch modes of the amide group in other molecules.[21] The $\Delta_{\mathrm{CO(thread)-NH}}$ cross anharmonicity arises from the 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.[22−25]

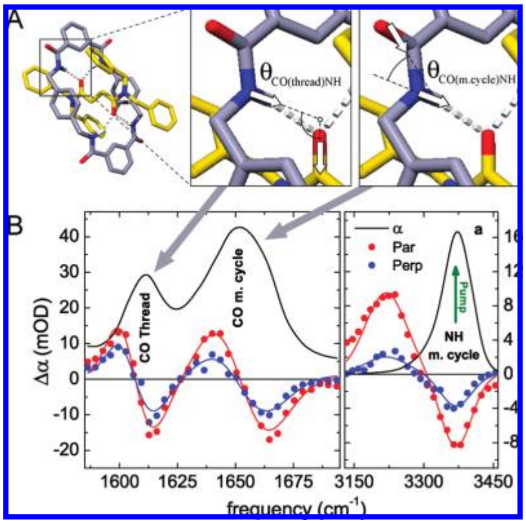

FIGURE 2. (A) Close-ups of the rotaxane shown in Figure 1A, showing the two angles that can be determined from the NH/CO(thread) and NH/CO(macrocycle) cross-anisotropies in the graph below. (B) Absorption spectrum (black curve) and transient-absorption change for parallel (red points) and perpendicular (blue points) pump−probe polarizations, upon pumping the NH-stretch mode (indicated by green arrow).

For the cross-peak anisotropies, we find $R_{\mathrm{CO(thread)-NH}} = 0.15$ and $R_{\mathrm{CO(macrocycle)-NH}} = 0.22$. These cross-peak anisotropies are directly related to the angle θ_{ij} between the transition-dipole moments of the coupled vibrations (see Figure 2A for the definition of these dipole−dipole angles). Using eq 1, we obtain angles $\theta_{\mathrm{CO(thread)-NH}} = 139°$ and $\theta_{\mathrm{CO(macrocycle)-NH}} = 33°$. Using the known angle of 20° between the amide I transition dipole and the C═O bond,[18] we obtain an angle $\angle(\mathrm{N{-}H,C{=}O_{macrocycle}})$ of ∼15°, close to the average value of 12° in the X-ray structure.[14] The other 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,[18] we predict an angle $\angle(\mathrm{N{-}H,C{=}O_{thread}})$ (indicated in Figure 2A) of 139° from the observed cross-peak anisotropy. This value again agrees

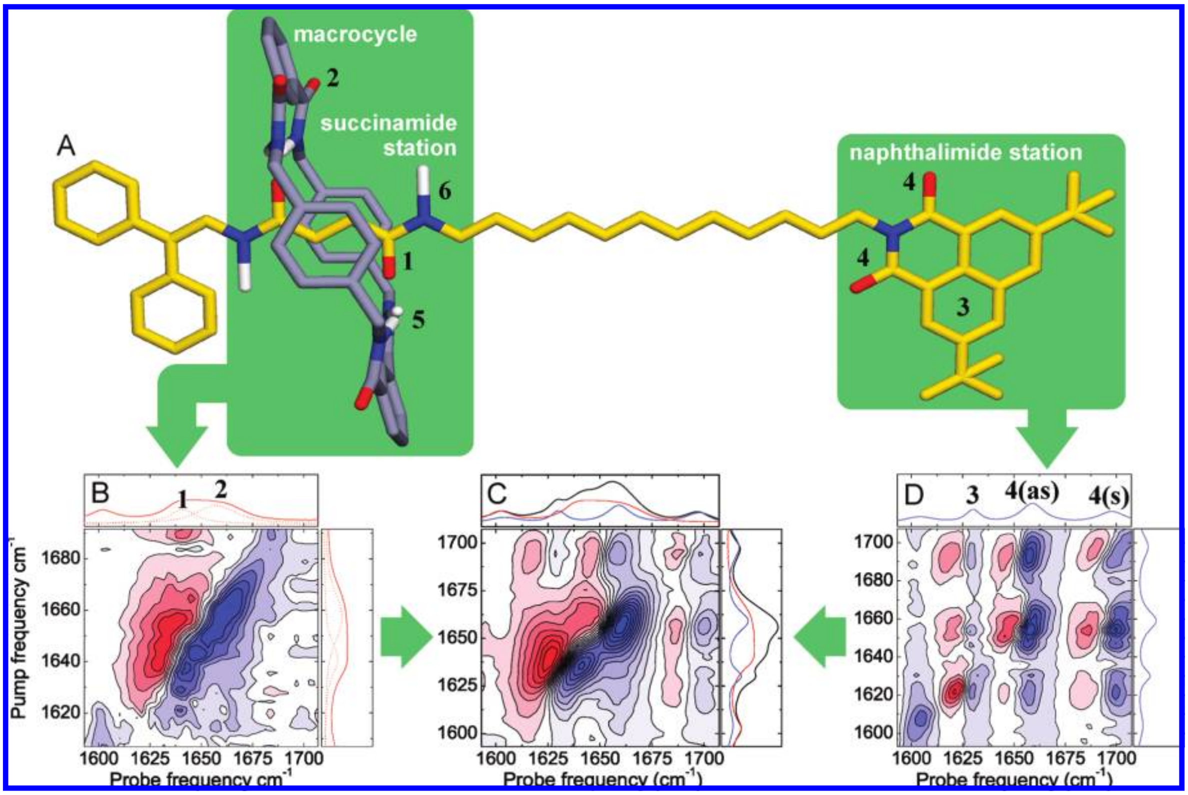

FIGURE 3. (A) Rotaxane-based molecular shuttle. Numbering of CO and NH groups matches that of the absorption peaks in panels B−D and in Figure 4. (B) 2D-IR spectrum of the left moiety of the shuttle. (C) 2D-IR spectrum of the complete shuttle. (D) 2D-IR spectrum of the naphthalimide moiety of the shuttle. s = symmetric and as = antisymmetric CO-stretching mode.

fairly well with the angle in the X-ray structure,[14] which is $\angle(\mathrm{N{-}H,C{=}O_{thread}}) = 114°$. Both the cross-anharmonicity and the cross-anisotropy are sensitive probes of the rotaxane co-conformation. Unlike the cross-anharmonicity however, the cross-anisotropy can be used to obtain quantitative information about the co-conformation of a rotaxane in a straightforward manner and without using model calculations.

Decomposing the 2D-IR Spectrum of a Molecular Shuttle

Rotaxane-based molecular machines are more complicated than the short symmetric rotaxane discussed above. Figure 3A shows a rotaxane-based shuttling device[20] that we have recently investigated. The thread of this rotaxane contains a succinamide and a naphthalimide station. In the electronic ground state, the macrocycle binds predominantly to the succinamide station (equilibrium constant for succinamide binding vs. naphthalimide 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 anion thus created are a much stronger hydrogen-bond acceptors than those of the succinamide station (the equilibrium constant for naphthalimide-anion binding vs. succinamide binding is >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.[20]

The shuttling involves subsequent breaking and formation of CO···NH hydrogen bonds and motion of CO groups with respect to each other. Since the macrocycle and the initial and final stations of the motion all contain CO groups (see Figure 3A), the departure and arrival of the macrocycle should be observable as the disappearance and appearance of specific CO/CO cross peaks in 2D-IR spectra. In addition, the formation of hydrogen bonds between the macrocycle and either of the stations should be observable as NH/CO cross peaks in a two-color 2D-IR spectrum. It should however be realized that such experiments will be more difficult than might be expected based on the simple 2D spectrum of the short rotaxane discussed so far. This is because the device has more CO-stretching modes than the short rotaxane, and additional IR-active naphthalimide aromatic ring-stretching modes in the same frequency region. To determine to what extent 2D-IR can be used to probe the co-conformation of the molecular shuttle, we have investigated the 2D-IR spectra of the neutral co-conformation (shown in Figure 3A) in detail.

We find that the CO/CO 2D-IR spectrum of the molecular shuttle, shown in Figure 3C, 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 separate parts of the molecular shuttle. Since the device consists of two halves (indicated by green boxes in Figure 3A) that do not interact, the 2D spectrum of the shuttle should be the sum of the 2D spectra of these two halves. This is confirmed by the data shown in Figure 3B–D. Figure 3B shows the absorption spectrum of the succinamide/macrocycle part. It consists of the absorption peak **1** of the succinamide CO-stretching mode and the absorption peak **2** of the macrocycle CO-stretching mode. The succinamide CO-stretching mode has a higher frequency in the molecular shuttle than in the rotaxane of Figure 1A because the CO groups are in a secondary instead of a tertiary amide group. As a consequence, the CO-stretch peaks 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 2D spectrum of the naphthalimide stopper is shown in Figure 3D. Its absorption spectrum contains three well-separated peaks, which arise from the symmetric (4s) and antisymmetric (4as) CO-stretching modes and from aromatic ring-stretch modes (3).[26] Each pair of modes gives rise to intense and well-separated cross peaks, leading to a total of six cross peaks, each of which has the positive–negative doublet structure discussed earlier. These cross peaks and their anisotropies are related to the intramolecular geometry of the naphthalimide stopper. For instance, from the 4s/4as cross peak, we can determine the angle between the CO groups in the naphthalimide group. Comparison of the 2D spectra of Figure 3B,D with that of 3C shows that the 2D spectrum of the rotaxane is indeed the sum of the spectra of the two constituent parts. Using the assignments of B and D, the spectrum of C can now be interpreted qualitatively. However, the overlap of some of the peaks (notably peaks **1** and **3**) makes it difficult to observe the corresponding cross-peaks separately. This makes it difficult to obtain quantitative information from the CO-stretching 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**.

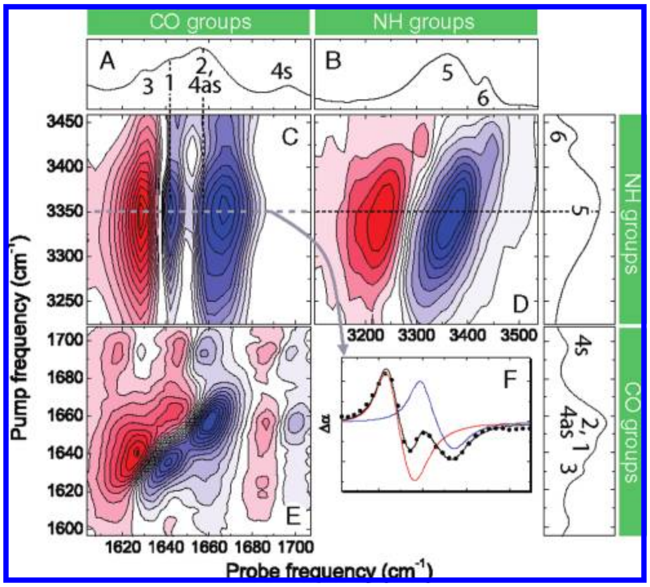

FIGURE 4. Multicolor 2D-IR spectrum of the molecular shuttle depicted in Figure 3A. Absorption peaks are numbered according to the corresponding CO and NH bonds as shown in Figure 3A: (A, B) absorption spectra in the NH- and CO-stretching regions; (C) NH/CO 2D spectrum; (D) NH/NH 2D spectrum; (E) CO/CO 2D spectrum; (F) horizontal cross section through panel C, as indicated by dashed gray line.

Multicolor 2D-IR Spectrum of a Molecular Shuttle

Because of the spectral congestion in the CO-stretching region, we investigated NH/NH and NH/CO couplings as alternative 2D-IR probes of the co-conformation of the molecular shuttle. Figure 4 shows the 2D-IR spectrum of the shuttle with a frequency range extended to cover both the NH- and CO-stretching modes. This extended 2D spectrum comprises three spectral regions in the (ν_{probe},ν_{pump}) domain: (ν_{CO},ν_{CO}) (shown in Figure 3C and discussed in the previous section), (ν_{NH},ν_{NH}), and (ν_{CO},ν_{NH}).

There are two NH-stretching peaks in the absorption spectrum of the molecular shuttle, see Figure 4B (for the numbering of absorption peaks and corresponding modes, see Figure 3A). These correspond to the NH groups in the macrocycle (5) and in the succinamide station of the thread (6). Each of the two NH-stretch peaks gives rise to a diagonal peak in the NH/NH 2D-IR spectrum (Figure 4D). These diagonal peaks have very different shapes: the contours of the succinamide NH-stretch mode at (3450, 3450) cm^{-1} are vertical, whereas those of the macrocycle NH stretch mode at (3300, 3300) cm^{-1} are tilted along the diagonal. Just like for the CO-stretch mode discussed above, this tilt reflects the width of the distribution of hydrogen-bond strengths of the rotaxane system in a quantitative manner.[17] The succinamide NH groups are not (or are weakly) hydrogen-bonded, and hence their stretch mode exhibits no spectral inhomogeneity. Because of the proximity of the succinamide and macrocycle NH groups, one might expect cross-peaks between the NH-stretch modes (which would be expected at (ν_{probe}, ν_{pump}) = (3300, 3450) and (3450, 3300) cm^{-1}), but these are so weak as to be obscured by the diagonal peaks. Using eq 2, one predicts a coupling of -1.3 cm^{-1} between the succinamide and macrocycle NH modes. Calculated NH/NH 2D spectra show that cross-peaks will only be visible when the coupling is on the order of 5 cm^{-1} or larger. Hence the NH/NH 2D spectrum is not well suited to obtain structural information on the macrocycle/thread co-conformation.

The heterovibrational NH/CO 2D spectrum (shown in Figure 4C) on the other hand does provide such structural information. The spectrum contains two NH/CO cross peaks, both for the same pump frequency of 3350 cm^{-1}. The positive half of the doublet structure of the right cross-peak is not visible, and the negative part of the left cross-peak is smaller than its corresponding positive part. This is due to overlap and consequent partial canceling of the two cross-peaks. A horizontal cross section through the 2D spectrum (shown in Figure 4F) shows how the observed response arises from the addition of the two cross-peaks. The left cross-peak arises from coupling between the macrocycle NH-stretch mode 5 and the CO stretch mode of the thread 1, and the right cross-peak arises from coupling between the macrocycle NH-stretch and macrocycle CO-stretch modes. Unlike the CO/CO 2D-IR spectrum, the NH/CO spectrum is not congested. This is because only those CO-stretch modes that are coupled to the NH-stretch mode show up in the NH/CO cross-peak region. When the macrocycle is at the succinamide station, exciting the macrocycle NH-stretch mode therefore gives a response only from the CO-stretch mode of the succinamide, and no response from the naphthalimide stopper (and vice versa when the macrocycle is at the naphthalimide station). The left NH/CO cross peak is due to coupling between the macrocycle NH and thread CO stretch modes. The magnitude of this coupling, and hence the cross-peak intensity, is determined by the macrocycle-NH/thread-CO distance and orientation. This cross peak is therefore ideally suited to probe the instantaneous position of the macrocycle on the thread, and its cross anisotropy can be used in the same manner as for the short rotaxane to determine directly the ring–thread orientation. The time resolution of this structural probe is the duration of the convolution of the pump and probe pulses, which is about 100 fs.

Concluding Remarks

Our results demonstrate that 2D-IR spectroscopy can be used to obtain quantitative information about the co-conformation of rotaxanes with subpicosecond 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 an NH-stretch and a 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. Application of 2D-IR spectroscopy to rotaxane-based molecular machines can be complicated because of the larger number of vibrational modes, which leads to spectral congestion. Heteronuclear 2D-IR provides an efficient way to circumvent this spectral congestion and probe the co-conformation in these larger rotaxanes as well.

Our results demonstrate the feasibility of time-resolved 2D-IR experiments in which externally triggered structural changes of molecular devices are measured with subpicosecond time resolution. Preliminary results on optically triggered shuttling of the rotaxane in Figure 3A have now been obtained.[27] In these UV-pump IR-probe experiments, the elementary events that underly the mechanical motion (departure from succinamide station, arrival at naphthalimide station) can be observed separately. This makes it possible to investigate the nature of the mechanical motions at the molecular level with unprecedented time resolution. Thus 2D-IR spectroscopy on molecular machines will lead to insights into their functioning that are difficult to obtain with other experimental methods.

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