Rotaxanes are almost always associated with the concept of molecular machines and have received considerable attention from nanoscience disciplines\(^1\). Rotaxanes are a subclass of mechanically interlocked architectures\(^2\). The name rotaxane comes from the Latin *rota* (wheel, green in figure 1 right) and *axis* (axle, black in figure 1 right), derived from the general structure of a rotaxane. The idea that rotaxanes could form the precursor of molecular machines comes from arguably the most interesting property of rotaxanes: the possibility for the movement of the macrocycle (wheel) from one station (red in figure 1 right) to the other on the thread (axle)\(^3,4\). Perhaps more modest switching applications are in data storage, information processing\(^4\), rearrangement of the structure of surfaces\(^5\) and transport across membranes\(^5\). The movement of the macrocycle between two or more stations has to be induced by an external stimulus. This movement of the “machinery” has been observed by various means, directly via X-ray studies and transient UV/VIS spectroscopy\(^3,5\) and indirectly via linear UV/VIS spectroscopy\(^6\). We have explored a direct means of following the motion of the macrocycle with fentosecond two dimensional infrared spectroscopy (2D-IR). This form of spectroscopy is a direct analogy to 2D NMR spectroscopy\(^7\). The coupling between two vibrationally excited chemical groups can be observed as cross-peaks in the two dimensional spectrum of the molecule. The rotaxane we investigated is the benzyllic amide rotaxane shown in figure 1.

We have opted to use the NH-stretch modes of the amide groups (NH) in the macrocycle and the thread of the rotaxane as a probe. The C=O stretch region of the spectrum has previously been investigated by Larsen et.al.\(^8\) but this part of the spectrum is too congested to be useful as a direct probe. The rotaxane was investigated in a specially built sample cell which allowed us to record infrared spectra in real-time whilst conducting electro chemistry. We hope to observe the cross peaks in the two-dimensional spectrum disappear as we let the macrocycle switch stations. If successful, this technique could prove a standard method of observing rotaxane motion.

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