

–Electronic Supporting Information– Time-Resolved Vibrational Spectroscopy of a Molecular Shuttle

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1 Experiment

The effective 355 nm pulse length is determined from the cross-correlation with the mid-IR pulse in a Ge plate (shown in Fig. S1). The data is fitted with a gaussian function (see curve) from which we obtain a full-width half-maximum (FWHM) of 3.6 ± 0.4 ns for the pump pulse.

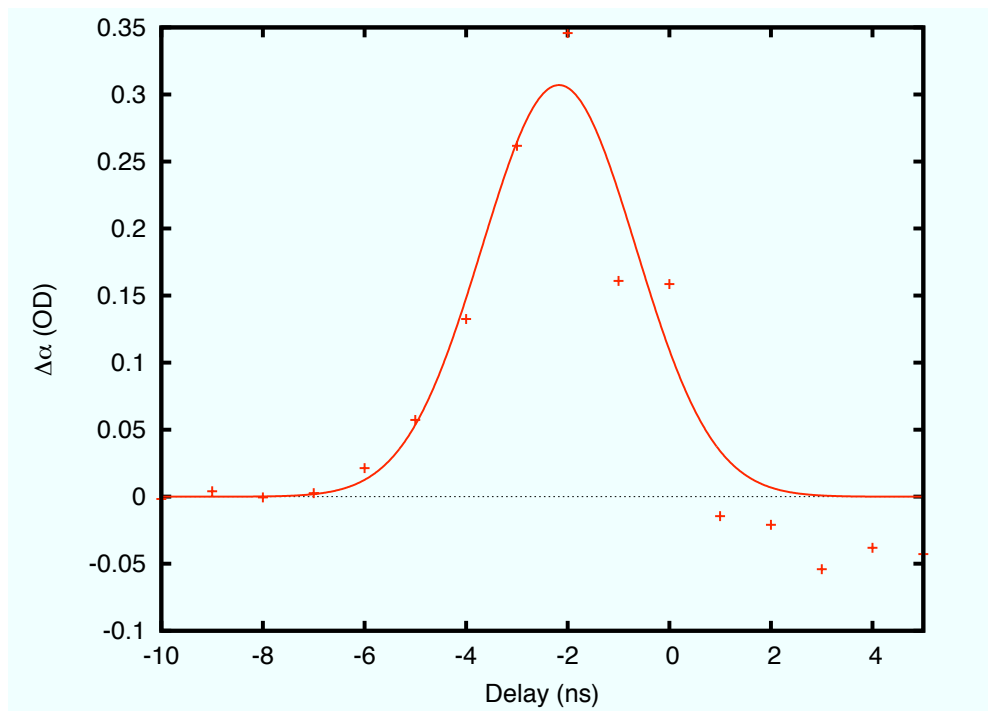


Figure S1 The cross-correlation of the of the mid-IR probe pulse and 355 nm pump pulse fitted with a gaussian function.

There are several considerations that need to be made in order to obtain the necessary signal strength and longevity. The concentration of **ni** station, whether it is part of a bare thread or rotaxane, affects the rates of radical anion creation and recombination. Both the reduction of the **ni** station by DABCO and the recombination of the **ni**^{•-} with the DABCO^{•+} are bimolecular processes. The former, however, is observed to be pseudo-first order because of the excess of DABCO ($\times 100$) used in the experiment. Increasing the concentration of the electron donor will result in an increased concentration of **ni**^{•-} station after 355 nm excitation. However, the rate at which the **ni**^{•-} recombines will also increase. The concentration of the rotaxane also has bearing on the concentration of **ni**^{•-} formed. One would expect that at high rotaxane concentrations, more **ni**^{•-} would be formed after 355 nm excitation. However, if the concentration of rotaxane is sufficiently high that the chance of two rotaxanes in the triplet state come into contact with one another is no longer negligible, triplet-triplet annihilation occurs. This leads to a lower concentration of

$\text{ni}^{\bullet-}$ and consequently less signal in our pump-probe experiments. CD_3CN has very little absorption in the region of interest, thus allowing for a 10 mm sample cell path length. We were therefore able to measure on solutions with a rotaxane concentration as low as 10^{-4} M.

In our previous study,¹ we use a bi-exponential function to perform a global least-squares fit of the normalized temporal evolution of peaks **5**, **11**, **15**, **16**, and **17**. The reduction of the **ni** by DABCO is a 2nd order reaction. However, due to the large excess of DABCO compared to the rotaxane, we can approximate the reduction with an exponential function. By normalizing on the intensity of peak **1**, we significantly limited the delay range we could use for data analysis. As the signal decreases in time due to recombination, the normalization introduces increasing quantities of extra noise. The signal measured at delays ≥ 3000 ns is useless when using this method.

2 Calculations

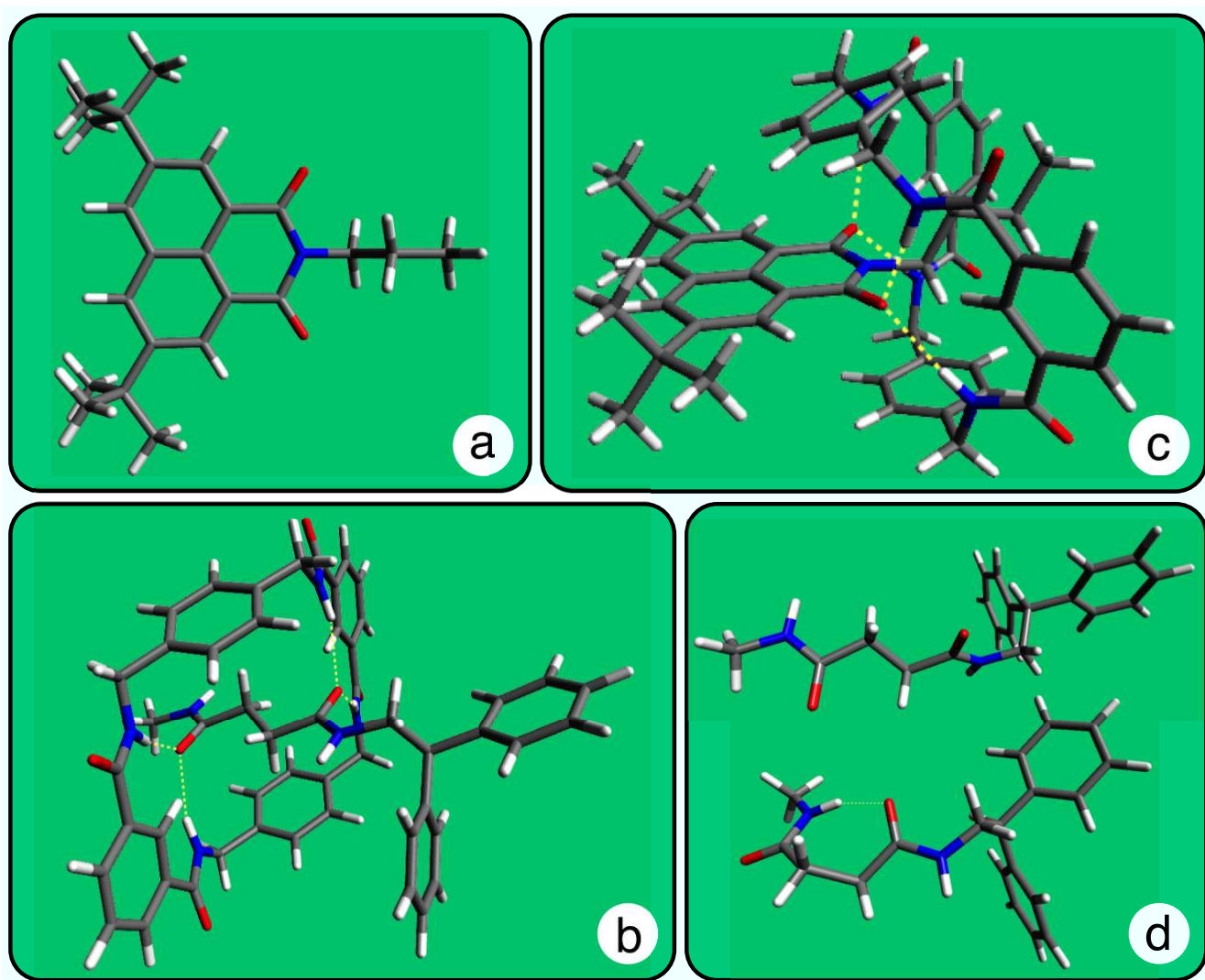


Figure S2 Model systems used to calculate the frequencies summarized in table 1 of the main text; panel **a**: *n*-propyl-naphthalimide station; panel **b**: methyl-succinamide station-macrocycle pseudo-rotaxane; panel **c**: radical anion *n*-propyl-naphthalimide station-macrocycle pseudo-rotaxane; panel **d**: free methyl-succinamide station in the free (top) and in the intramolecular hydrogen-bonded (bottom) state. The yellow dashed lines represent hydrogen bonds. The labeling corresponds to that used in table 1, main text.

3 Singular Value Decomposition

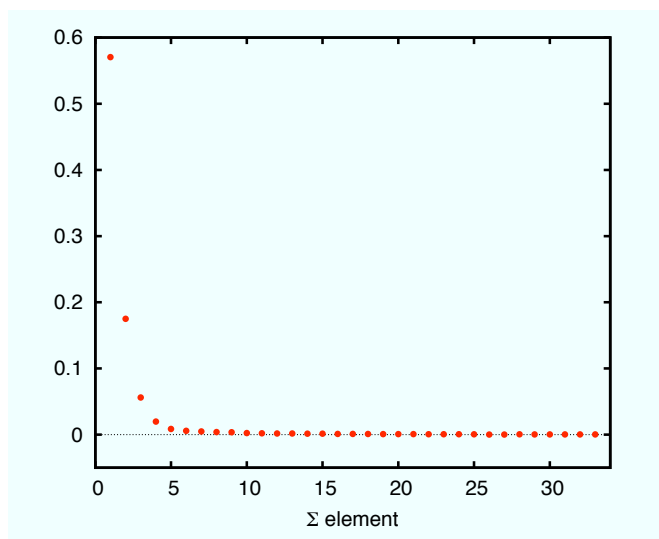


Figure S3 Weights of the principal components obtained from the SVD.

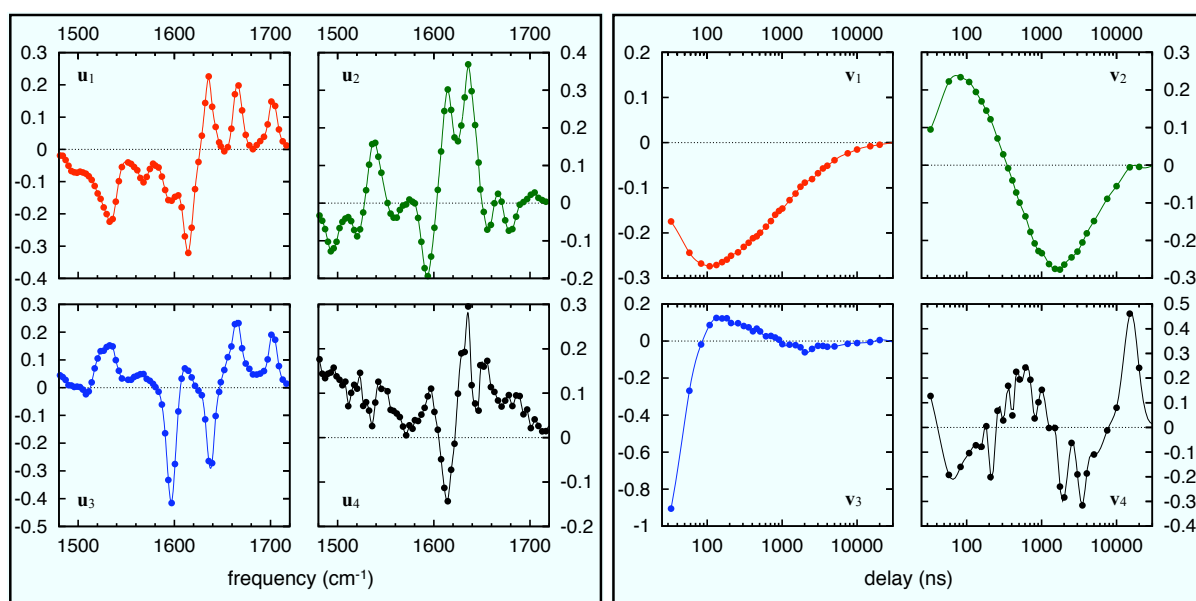


Figure S4 Left: The first four projection vectors of the SVD. Right: The first four target vectors of the SVD.

4 Kinetic Model

This section contains the mathematica code for the numerical integration of the kinetic differential equations and their proposed solutions.

```

(* define Ansatz functions;
   X = triplet conc.
   A = total anion conc.
   Y = conc. anion before shuttling
   Z = conc. anion after shuttling
*)

Xt[t_] := NO * Exp[-kT * t];
At[t_] := (1 - Exp[-kT * t]) * kQ / (Exp[kQ * t] * (kQ / (η * NO) + kR) - kR);
Yt[t_] := (kT / (kT - kQ - kS)) * (Exp[-(kQ + kS) * t] - Exp[-kT * t]) / ((1 / (η * NO)) + kR * t);
Zt[t_] := At[t] - Yt[t];

(* Simplify last expression to get eq. as in the text *)

zt[t]


$$\frac{(1 - e^{-t k_T}) k_Q}{-k_R + e^{t k_Q} \left( \frac{k_Q}{NO \eta} + k_R \right)} - \frac{(e^{t(-k_Q - k_S)} - e^{-t k_T}) k_T}{\left( \frac{1}{NO \eta} + t k_R \right) (-k_Q - k_S + k_T)}$$


(* Define values of rate constants and NO. *)

kT = 0.0390543;
kS = 0.00129337;
kR = 9;
kQ = 5.33369 * 10^(-5);
NO = 29.8702 * 10^(-5);
η = 0.2;

(* Calculate "exact" solution of differential eqs. numerically: *)

Clear[sol];
sol =
NDSolve[{X'[t] == -kT * X[t], Y'[t] == η * kT * X[t] - kS * Y[t] - kR * Y[t] * (Y[t] + Z[t]) - kQ * Y[t],
         Z'[t] == kS * Y[t] - kR * Z[t] * (Y[t] + Z[t]) - kQ * Z[t],
         X[0] == NO, Y[0] == 0, Z[0] == 0}, {X, Y, Z}, {t, 0, 30000}]

{{X → InterpolatingFunction[{{0., 30000.}}, <>],
  Y → InterpolatingFunction[{{0., 30000.}}, <>],
  Z → InterpolatingFunction[{{0., 30000.}}, <>]}}

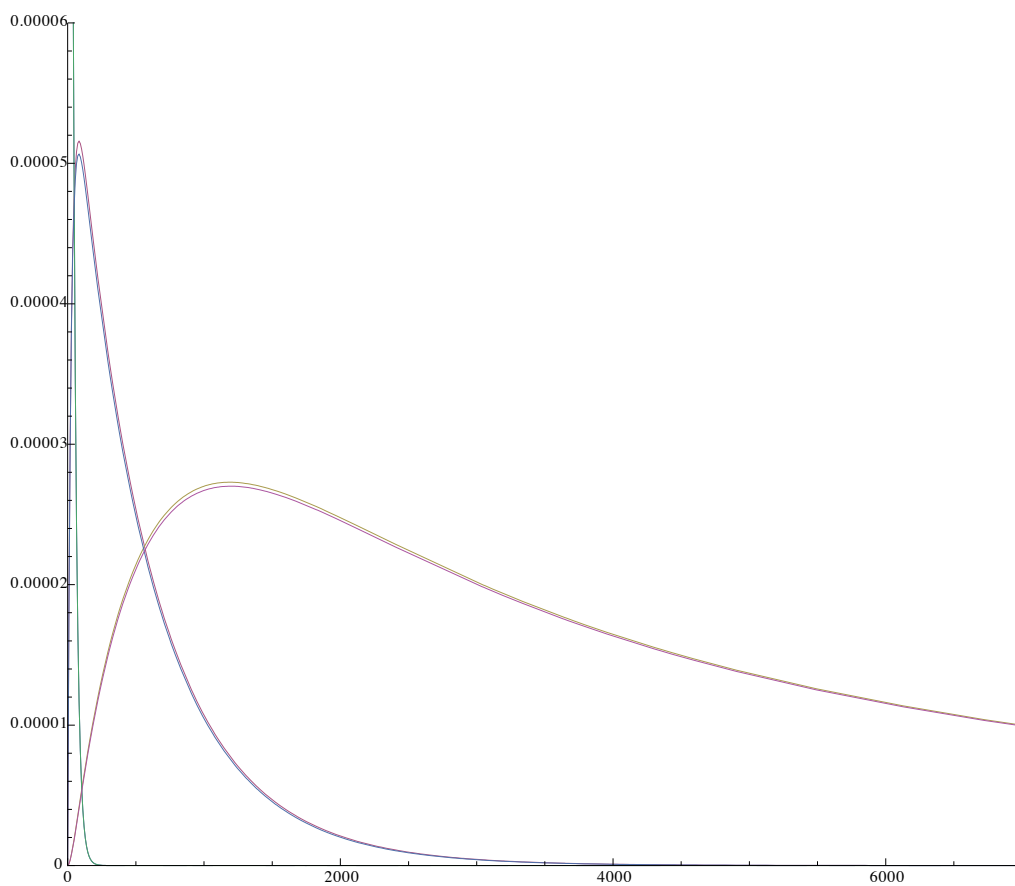
X[1.] /. sol
{0.000287261}

(* Compare results for Y and Z (for X the 'Ansatz' is simply the exact solution!!) *)

```

2 | *ansatz_func_accuracy.nb*

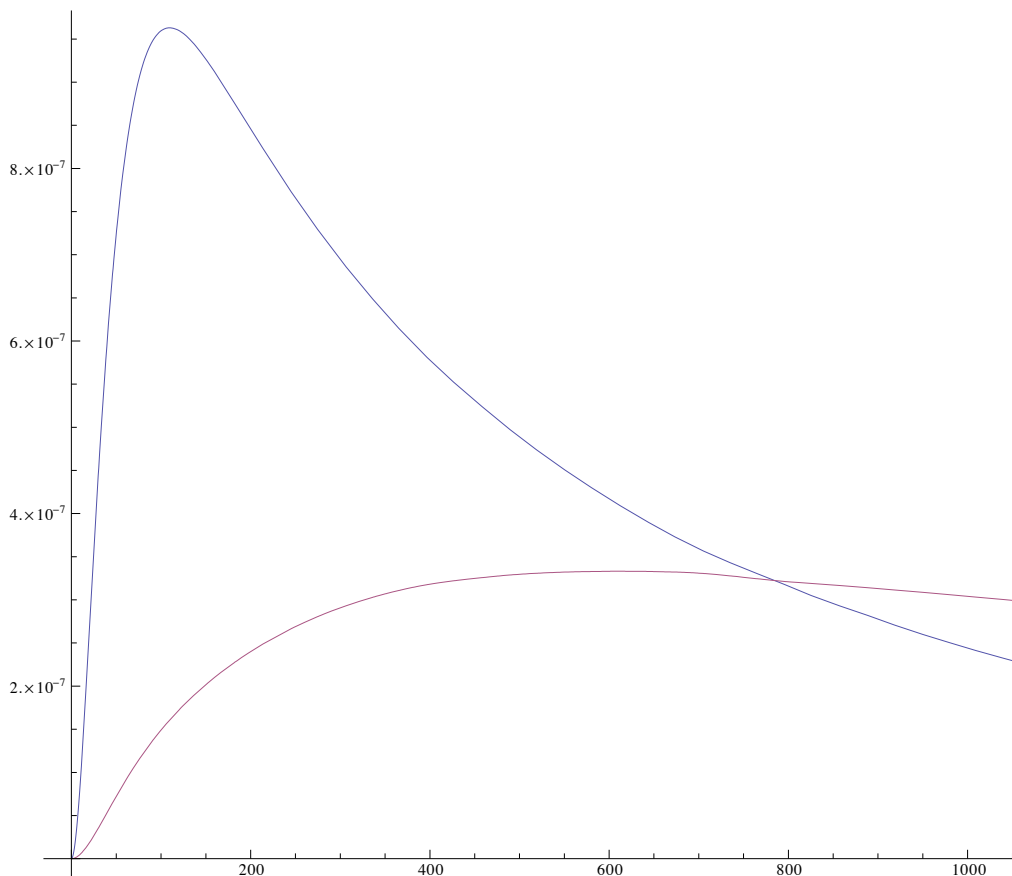
```
Plot[{Evaluate[X[t] /. sol], Evaluate[Y[t] /. sol], Evaluate[Z[t] /. sol],  
      Xt[t], Yt[t], Zt[t]}, {t, 0, 30000}, PlotRange -> {{0, 10000}, {0, 0.00006}}
```



(* Plot the deviations between Ansatz and exact solution for Y and Z *)

§


```
Plot[{Abs[Yt[t] - (Y[t] /. sol)], Abs[Zt[t] - (Z[t] /. sol)]}, {t, 0, 1500}]
```



```
(* Find the time at which maximum deviation  
between Ansatz and exact solution occurs for Y: *)
```

```
tmaxdev = t /. Last[FindMaximum[Abs[Yt[t] - (Evaluate[Y[t] /. sol])], {t, 50}]]
```

```
109.384
```

```
(* determine the relative value of the maximum deviation: *)
```

```
relmaxdev = Abs[Yt[tmaxdev] - (Y[tmaxdev] /. sol)] / (Y[tmaxdev] /. sol)
```

```
{0.0190397}
```

```
Plot[Abs[Zt[t] - (Evaluate[Z[t] /. sol])], {t, 0, 2000}]
```

```
(* The same, now for Z: *)
```

```
tmaxdev = t /. Last[FindMaximum[Abs[Zt[t] - (Evaluate[Z[t] /. sol])], {t, 500}]]
```

```
609.832
```

```
relmaxdev = Abs[Zt[tmaxdev] - (Z[tmaxdev] /. sol)] / (Z[tmaxdev] /. sol)
```

```
{0.0141424}
```

References

- [S1] M. R. Panman, P. Bodis, D. J. Shaw, B. H. Bakker, A. C. Newton, E. R. Kay, D. A. Leigh, A. M. Brouwer, W. J. Buma and S. Woutersen, *Science*, 2010, **328**, 1255–1258.