

Conformational Flexibility of a Rotaxane Thread Probed by Electronic Spectroscopy in Helium Nanodroplets

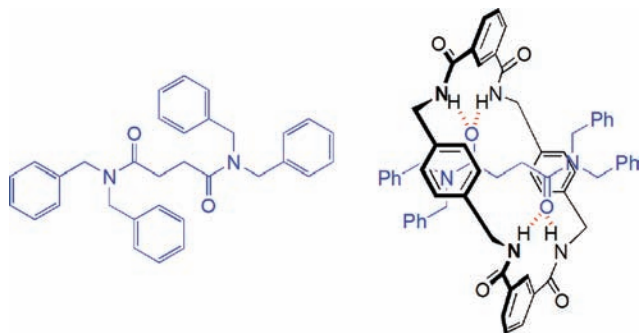
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Mechanically interlocked architectures such as rotaxanes are multicomponent assemblies that hold great promise for a molecular, bottom-up approach toward nanotechnological applications.^{1,2} Conformational dynamics are at the very heart of the interesting properties of these molecular-level machines. Yet questions such as how to characterize the large degree of conformational heterogeneity intrinsically present in these systems and how this heterogeneity influences their properties, as well as questions on how intercomponent interactions affect the conformational flexibility of each of the components have so far not been systematically addressed.

Chart 1. Chemical Structure of Succinamide Thread **1** and the Rotaxane Architecture Employed to Shape Thread **1**³



Recently, we showed that high-resolution spectroscopy in combination with molecular beam methods provides an excellent means to answer such questions.^{3,4} In particular, we used these techniques to demonstrate how one can employ the rotaxane architecture to force an encapsulated and interlocked molecular structure—in that case a thread containing a succinamide binding motif (Chart 1)—into a specific shape, and control, change, and decrease the number of conformations it can adopt.³ In these experiments individual conformations of thread **1** could not be distinguished because of the limited cooling capabilities of molecular beams for larger molecules. The width of the spectral lines in the excitation spectrum was thus determined by conformational heterogeneity and possibly hot bands. Here we report on the first spectroscopic studies of thread **1** that do enable observation and characterization of its individual conformations, and thus show their potential for detailed studies of the conformational structure and dynamics of molecular devices and their building blocks.

In our experiments thread **1** is embedded in liquid helium droplets having a temperature of 0.38 K and consisting on average of 20,000 helium atoms. Electronic spectra of cold molecules are recorded by monitoring as a function of laser frequency the number of free ions created via a $1 + 1'$ resonance enhanced two-photon ionization (REMPI) scheme.^{5,6}

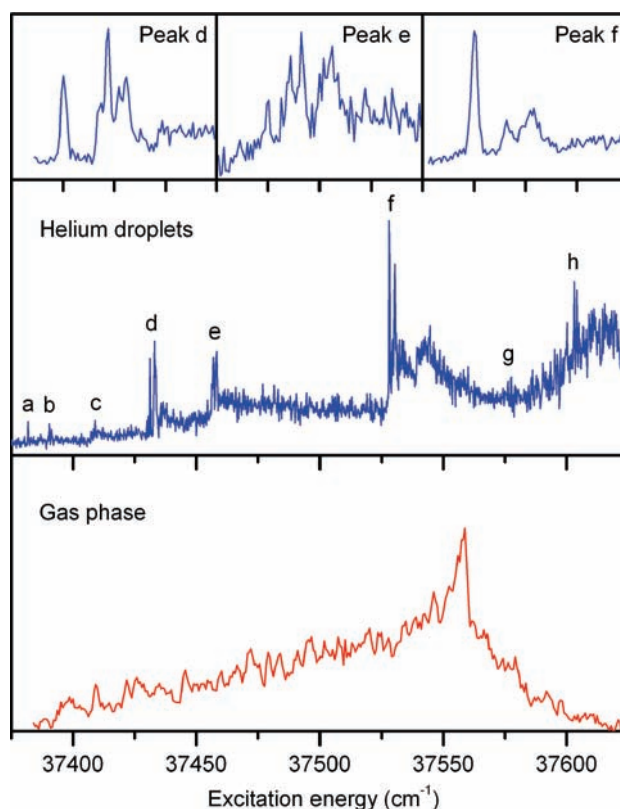


Figure 1. REMPI excitation spectrum of succinamide thread **1** obtained in a liquid helium matrix (middle panel) and seeded in an Ar supersonic beam (lower panel). Eight zero phonon lines corresponding to different conformers are observed at (a) 37382 cm⁻¹, (b) 37390 cm⁻¹, (c) 37407 cm⁻¹, (d) 37431 cm⁻¹, (e) 37455 cm⁻¹, (f) 37528 cm⁻¹, (g) 37576 cm⁻¹, (h) 37603 cm⁻¹. A detailed view covering 8 cm⁻¹ of three representative zero phonon lines is presented in the upper panel.

The middle panel of Figure 1 displays the excitation spectrum of thread **1** in helium droplets in the region of the S₁ band origin. The same figure shows for comparison the excitation spectrum under conditions that thread **1** is seeded by laser desorption into a supersonic beam expansion of Ar (lower panel). In the helium droplet spectrum a number of sharp resonances (zero phonon lines)

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with a fwhm of $\sim 0.4\text{ cm}^{-1}$ are observed. To confirm that the observed narrow lines are associated with monomers and do not in part derive from dimers, the dimer excitation spectrum was measured separately. In the wavelength range of interest this spectrum contains only two broad features with a fwhm of about 50 cm^{-1} around 37540 cm^{-1} and 37610 cm^{-1} . The same features are visible in the monomer spectrum, giving evidence for photo-dissociation of the dimer.

Comparison of the two spectra in Figure 1 shows that the strongest resonance in the helium droplet spectrum is displaced by -30 cm^{-1} with respect to the peak in the molecular beam spectrum. This shift closely follows what has been observed before for the excitation spectra of other organic molecules.⁷ It is the net result of a red shift arising from solvation of the molecule in a polarizable environment, and a blue shift due to the expansion of the solvation shell upon excitation. When we take the 30 cm^{-1} shift into account, we come to the conclusion that all of the features observed in the helium droplet spectrum fall within the excitation range spanned by the asymmetric resonance in the molecular beam spectrum. This strongly suggests that the resonances observed in liquid helium droplets are also present in the molecular beam spectrum of the thread. However, due to insufficient cooling of the sample molecules, the lines there cannot be resolved as separate features and appear in the spectrum as part of the broad tail.

While for most molecular systems the narrow zero phonon lines (ZPLs) and not the broad phonon wings (PWs) are the most prominent features in the spectrum,⁷ we and others have observed that, for flexible systems where electronic excitation can lead to substantial rearrangement of the molecule, the PWs are often much stronger than the ZPLs.^{5,8} It is thus quite remarkable—considering the flexibility inherent to thread **1**—that we mainly observe ZPLs. We take this as evidence that no significant geometry change takes place upon electronic excitation. Consequently, we do not expect a low-frequency vibrational progression and assign the ZPLs to different conformers. The fact that the spectrum shows no regular structure supports this assumption.

Closer inspection of the bands in the helium droplet spectrum reveals that in all cases the ZPL is not a single narrow resonance but is split into a multiplet (top panel Figure 1). This splitting can be attributed to the presence of more than one structural arrangement of helium atoms around thread **1**.^{7,9} In view of the multiple binding sites for helium present in thread **1**, it is not so surprising that various low-energy configurations are possible to localize helium atoms on the surface of the molecule. Interestingly, we find, however, that the number of lines into which each of the ZPLs is split and the intensity distribution over the multiplet is different for each ZPL. We take this as additional evidence for the existence of different conformers. In combination with quantum chemical calculations, this splitting and intensity distribution could serve as a unique spectral signature and offer a powerful means to identify the specific details of the conformational structure. Alternatively, IR–UV ion dip spectroscopy could be another experimental means to recover those details.⁴ This approach is presently being pursued.

By comparing the gas phase and droplet spectrum it is evident that the molecular beam spectrum is not simply a broadened version of the droplet spectrum. In particular, we observe that the three resonances at 37431 , 37455 , and 37603 cm^{-1} in the droplet spectrum have smaller amplitudes in the molecular beam spectrum, while in the 37490 – 37520 cm^{-1} region of the droplet spectrum one would have expected the presence of one or more conformers. These observations imply that the population distribution over the

accessible conformers in the helium droplet experiment is different from the one in the molecular beam experiment, although there is no indication that different conformers are accessed in the two experiments. Such differences in the relative contribution of conformers and suppression of particular conformers in helium droplets has been observed before for conformationally flexible systems.^{10,11} It is generally assumed that the different cooling dynamics in supersonic beams and helium droplets are (partly) responsible, but as yet it is still a not fully understood phenomenon.

In the helium droplet spectrum eight different conformations are observed. This number agrees quite nicely with results of molecular dynamics calculations on the conformational landscape of thread **1**.³ These calculations show that about 10 conformations lie within 1 kcal/mol and about 25 within 1.5 kcal/mol , energies that bracket the range for which we still expect to be able to observe conformations under our experimental conditions.

Summarizing, we have shown for the first time that it is possible to obtain ultrahigh resolution excitation spectra of a conformationally flexible succinamide-based thread, one of the binding motifs commonly employed in mechanically interlocked assemblies. This has enabled us to confirm and extend the conclusions of previous molecular beam experiments on the presence of many energetically close-lying conformations, and to identify the contribution of each distinct conformation to the spectrum. We believe that application of this approach to more complex [2]rotaxanes, and in particular to switchable systems, will lead to insight into—and ultimately control over—the functioning of such molecular devices.

Acknowledgment. This work was supported by The Netherlands Organization for Scientific Research (NWO) and the Swiss National Science foundation through Grant No. 200020-119789. Further financial support from EU projects *Hy3M* and *STAG* is gratefully acknowledged. A.M.R. acknowledges The Netherlands Organization for Scientific Research (NWO) for a VENI postdoctoral fellowship. The EPFL is acknowledged for additional financial support.

References

- (1) (a) Sauvage, J.-P.; Dietrich-Buchecker, C. *Molecular Catenanes Rotaxanes and Knots: A Journey Through the World of Molecular Topology*; Wiley-VCH: Weinheim, 1999. (b) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133. (c) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurlpel, G. W. *H. Science* **2001**, *291*, 2124. (d) Thordarson, P.; Bjsterveld, E. J. A.; Rowan, A. E.; Nolte, R. J. M. *Nature* **2003**, *424*, 915. (e) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845. (f) Berná, J.; Leigh, D. A.; Lubomska, M.; Mendoza, S. M.; Perez, E. M.; Rudolf, P.; Teobaldi, G.; Zerbetto, F. *Nat. Mater.* **2005**, *4*, 704. (g) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; Johnston-Halperin, E.; DeIonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shik Shin, Y.; Tseng, H.-R.; Stoddart, J. F.; Heath, J. R. *Nature* **2007**, *445*, 414. (h) Serreli, V.; Lee, C.-F.; Kay, E. R.; Leigh, D. A. *Nature* **2007**, *445*, 523. (i) Lee, C.-F.; Leigh, D. A.; Pritchard, R. G.; Schultz, D.; Teat, S. J.; Timco, G. A.; Winnepenny, R. E. P. *Nature* **2009**, *458*, 314.
- (2) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed* **2007**, *46*, 72 and references therein.
- (3) Rijs, A. M.; Crews, B. O.; Vries, M. S.; Hannam, J. S.; Leigh, D. A.; Fantì, M.; Zerbetto, F.; Buma, W. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 3174–3179.
- (4) Rijs, A. M.; Compagnon, I.; Oomens, J.; Hannam, J. S.; Leigh, D. A.; Buma, W. J. *J. Am. Chem. Soc.* **2009**, *131*, 2428.
- (5) Loginov, E.; Rossi, D.; Drabbel, M. *Phys. Rev. Lett.* **2005**, *95*, 163401.
- (6) (a) Braun, A.; Drabbel, M. *J. Chem. Phys.* **2007**, *127*, 114303. (b) Loginov, E.; Drabbel, M. *J. Phys. Chem. A* **2007**, *111*, 7504.
- (7) Stienkemeier, F.; Vilesov, A. F. *J. Chem. Phys.* **2001**, *115*, 10119.
- (8) Pentlehn, D.; Slenczka, A. Private communication.
- (9) (a) Kwon, Y.; Whaley, K. B. *J. Chem. Phys.* **2001**, *114*, 3163. (b) Birer, Ö.; Moreschinib, P.; Lehmann, K. K. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1648.
- (10) Lindinger, A.; Toennies, J. P.; Vilesov, A. F. *J. Chem. Phys.* **1999**, *110*, 1429.
- (11) Pei, L.; Zhang, J.; Wu, C.; Kong, W. *J. Chem. Phys.* **2006**, *125*, 024305.

JA905973V