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Melting of a beta-Hairpin Peptide Using Isotope-Edited 2D IR Spectroscopy and Simulations

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SUPPORTING INFORMATION

for

Melting of a β -hairpin peptide using isotope-edited 2D IR spectroscopy and simulations

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Cambridge, MA 02139 USA

Santanu Roy, Thomas L. C. Jansen, and Jasper Knoester

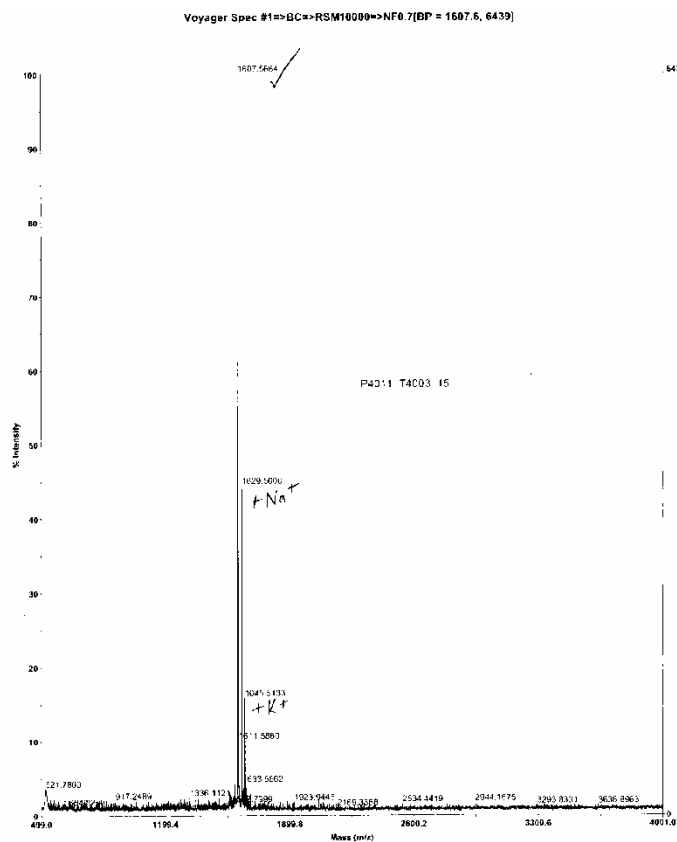
Center for Theoretical Physics and Zernike Institute for Advanced Materials, University of
Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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6. 2D IR spectral simulations for single structures

1. Mass spectra of the synthesized peptides

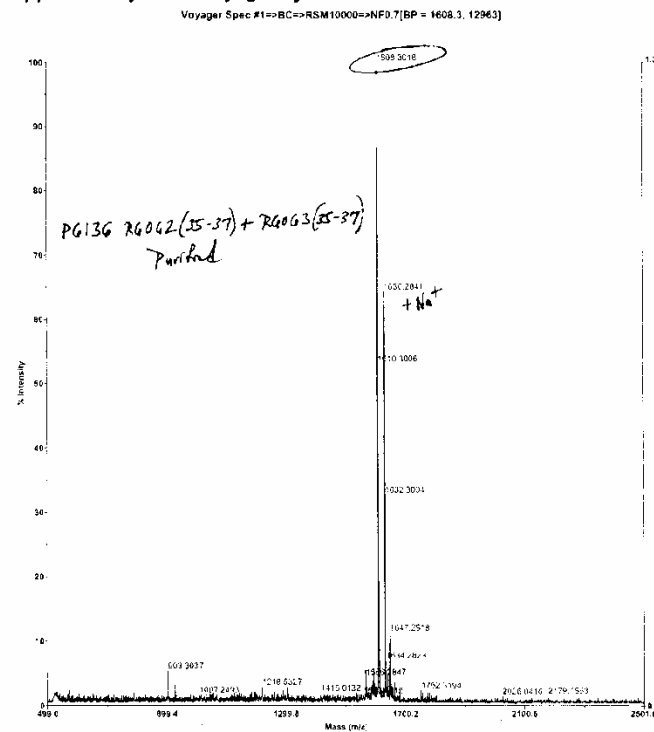
1.a. TZ2-UL mass spectrum recorded on an Applied Biosystems Voyager MALDI-TOF mass spectrometer on February 3, 2004. The expected mass of TZ2-UL is 1608 g/mol, and the recorded mass is 1607.6 g/mol.



DL_P4011_T4003_15.dat
Acquired: 7:54:00, February 03, 2004

1.b. TZ2-K8 mass spectrum recorded on an Applied Biosystems Voyager MALDI-TOF mass spectrometer on November 21, 2006. The expected mass of TZ2-K8(¹³C) is 1609 g/mol. The recorded mass is 1608.3 g/mol, which is approximately 1 a.m.u. higher than the recorded mass of TZ2-UL (Fig. 2.a.1).

Applied Biosystems Voyager System 4219



Mode of operation:	Reflector
Extraction mode:	Delayed
Polarity:	Positive
Acquisition control:	Manual
Accelerating voltage:	20000 V
Grid voltage:	66%
Mirror voltage ratio:	1.12
Guide wire D:	0%
Extraction delay time:	175 nsec
Acquisition mass range:	500 - 2500 Da
Number of laser shots:	50/spectrum
Laser intensity:	1700
Laser Rep Rate:	< 8 Hz
Calibration type:	External - D:\Maldi_data\2006\Nov
Calibration matrix:	α-Cyano-L-hydroxyisobutyric acid
Low mass gate:	500 Da
Timed ion selector:	Off
Digize! start time:	32.781
Bin size:	0.5 nsec
Number of data points:	80753
Vertical scale D:	7000 mV
Vertical offset:	0%
Input bandwidth:	750 MHz
Sample well:	21
Plate ID:	BIOPOLY1
Serial number:	4219
Instrument name:	Voyager-DE STR
Plate type / Reagent:	C:\VOYAGER\13C_well_plate.plt
Lab name:	MIT BIOPOLYMERS
Absolute x-position:	3749.77
Absolute y-position:	38680.5
Relative x-position:	216.27
Relative y-position:	1532.57
Shot in spectrum:	53
Source pressure:	1.582e-007
Mirror pressure:	1.99e-008
TC2 pressure:	0.02032
TIS gate width:	8
TIS flight length:	1161

Acquired: 09:15:00, November 21, 2006

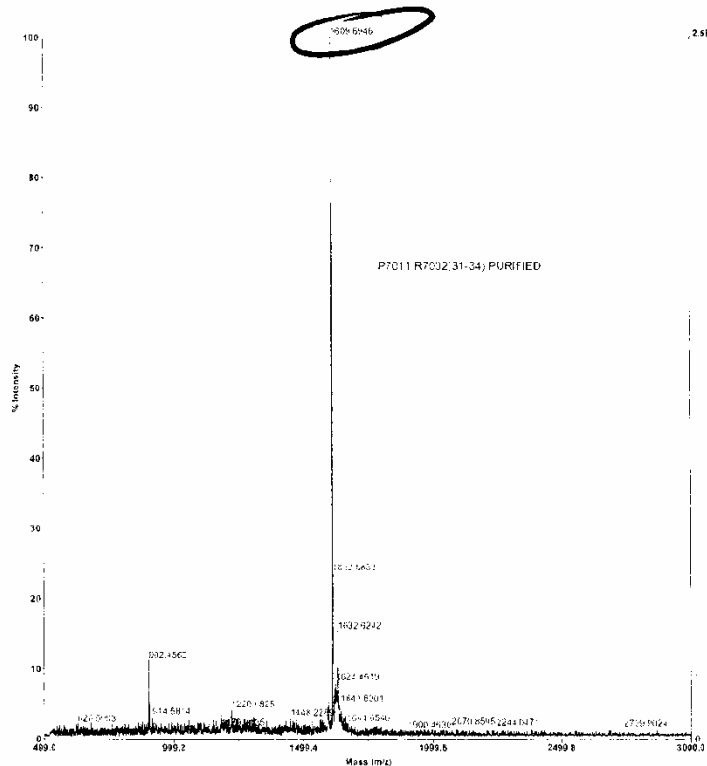
D:\Maldi_data\2006\Nov\200611-2108\p6136pur.dat

Printed: 09:16

1.c. TZ2-S1 mass spectrum recorded on an Applied Biosystems Voyager MALDI-TOF mass spectrometer. The expected mass of TZ2-S1(¹⁸O) is 1610 g/mol. The recorded mass is 1609.6 g/mol, which is approximately 2 a.m.u. higher than the recorded mass of TZ2-UL.

Applied Biosystems Voyager System 4219

Voyager Spec #1=>BC=>RSM1000=>NF0 7 [RP = 1609.7, 25228]



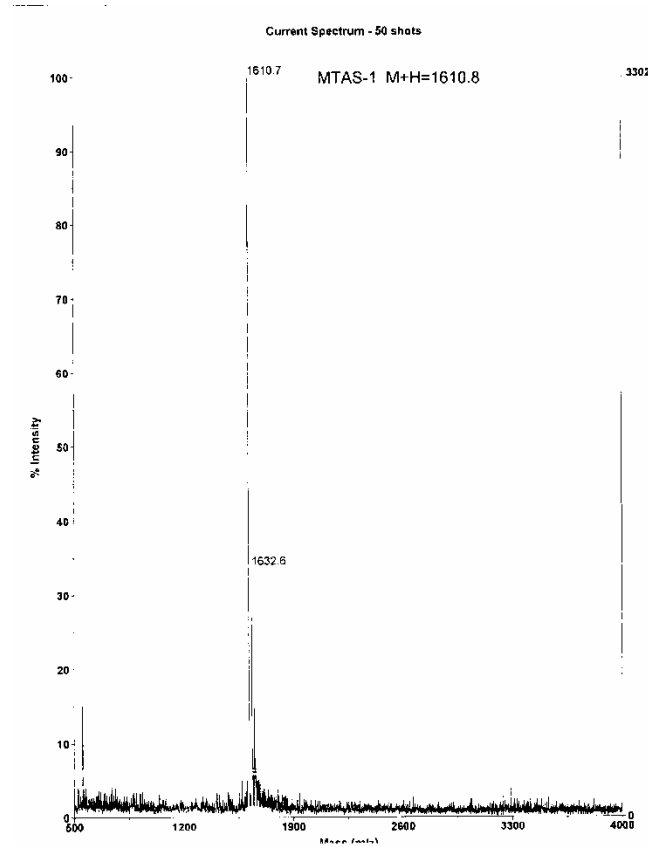
Mode of operation: Reflecter
 Extraction mode: De ayeo
 Polarity: Positive
 Acquisition control: Manual
 Accelerating voltage: 20000 V
 Grid voltage: 804
 Mirror voltage ratio: 1.12
 Guide wire 0: 0%
 Extraction delay time: 175 nsec
 Acquisition mass range: 500 -- 5000 Da
 Number of laser shots: 50-spectrum
 Laser intensity: 1904
 Laser Rep Rate: 2.7 Hz
 Calibration type: Externa -- D:\Maldi data\2007\Febr
 Calibration matrix: a-Cyano-4-hydroxycinnamic acid
 Low mass gate: 500 Da
 Timed ion selector: Off
 Digitizer start time: 32.762
 Bin size: 0.5 nsec
 Number of data points: 141253
 Vertical scale 0: 1000 mV
 Vertical offset: 0%
 Input bandwidth 0: 750 MHz
 Sample well: 97
 Plate ID: BIOPOLY2
 Serial number: 4219
 Instrument name: Voyager-DE STR
 Plate type filename: C:\VOYAGER\100 well plate.plt
 Lab name: MIT BIOPOLYMERS
 Absolute x-position: 32312.1
 Absolute y-position: 1146.26
 Relative x-position: 244.628
 Relative y-position: -441.237
 Shots in spectrum: 12
 Source pressure: 9.7 e-006
 Mirror pressure: 1.67 e-006
 TG2 pressure: 0.02164
 TIS gate width: 8
 TIS flight length: 1161

Acquired 11:12:00, February 22, 2007

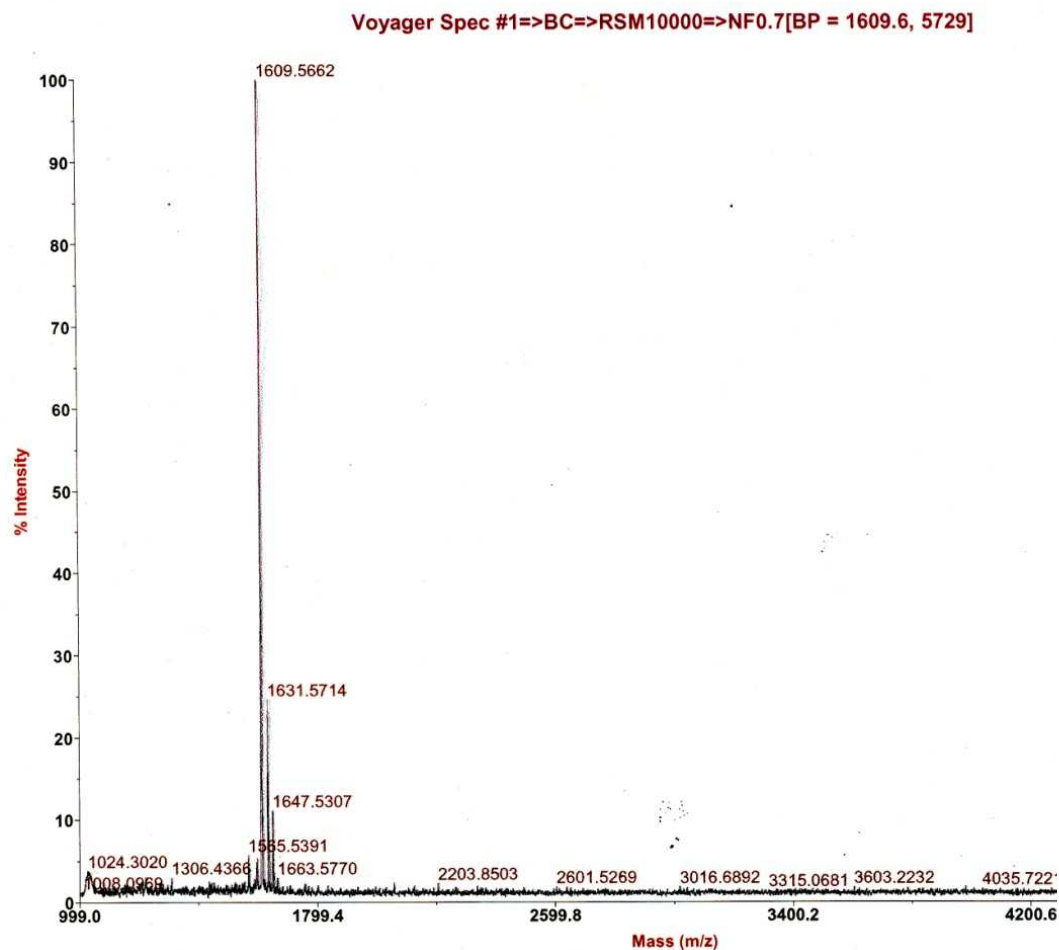
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Printed: 11:1

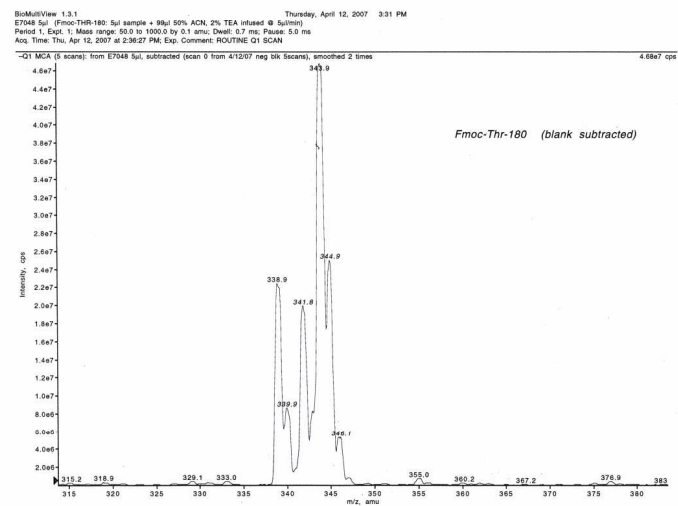
1.d. TZ2-TT mass spectrum provided by Anaspec Inc. The expected mass of TZ2-T3(¹³C)T10(¹³C) is 1610 g/mol, which agrees with the recorded mass of 1610.7.



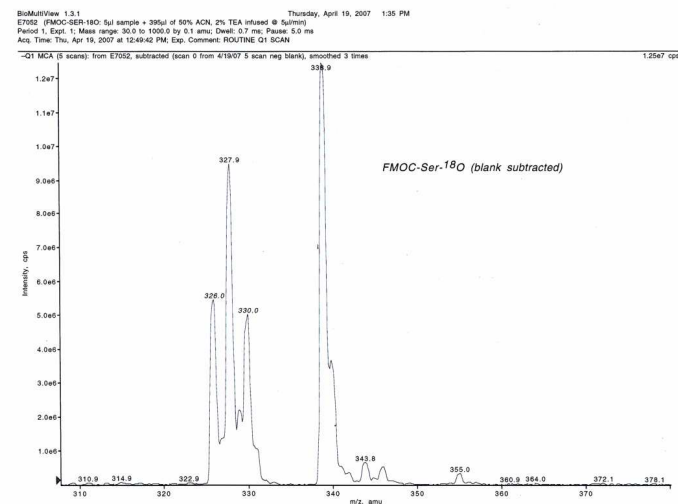
1.e. TZ2-T10 mass spectrum recorded on an Applied Biosystems Voyager MALDI-TOF mass spectrometer. The expected mass of TZ2-T10(¹⁸O) is 1610 g/mol. The recorded mass is 1609.6 g/mol, which is approximately 2 a.m.u. higher than the recorded mass of TZ2-UL.



D:\...T8026(36_41) T2Z.dat
Acquired: 18:33:00, October 21, 2008



1.f. ¹⁸O labeled Fmoc-Thr-OH mass spectrum recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS). The expected mass of unlabeled Fmoc-Thr-OH is 341.4 g/mol. The recorded masses are 341.8, 343.9, 344.9, and 346.1 g/mol. These masses represent a distribution in isotope label incorporation into Fmoc-Thr-OH.

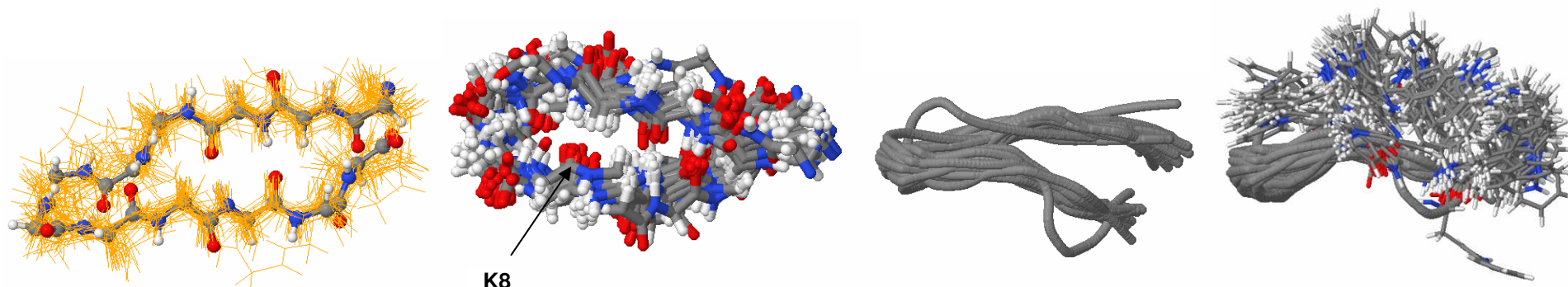


1.g. ¹⁸O labeled Fmoc-Ser-OH mass spectrum recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS). The expected mass of unlabeled Fmoc-Ser-OH is 327.3 g/mol. The recorded masses are 326.0, 327.9, and 330.0 g/mol. These masses represent a distribution in isotope label incorporation into Fmoc-Ser-OH.

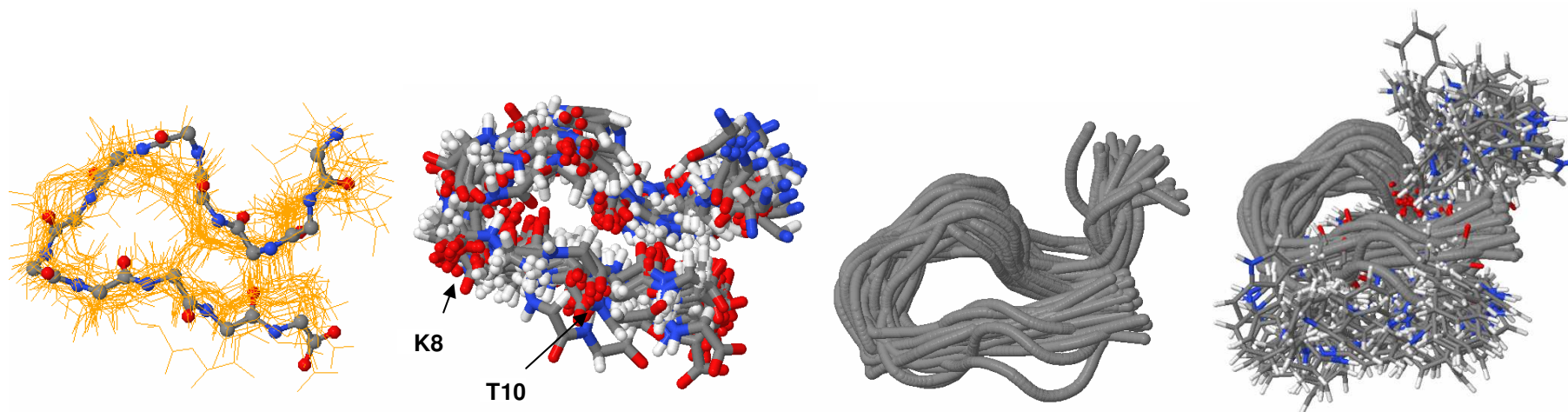
2. Visualization of the Markov States: Backbone conformation and tryptophan packing

Here we provide different visualizations of TZ2 for the 30 initial structures within each simulated Markov state. Backbone visualizations serve to characterize the amide group orientations and conformational disorder of each state, and the right panel illustrates the packing of tryptophans for each state. Structures are oriented in a manner that coincides roughly with Fig. 9.

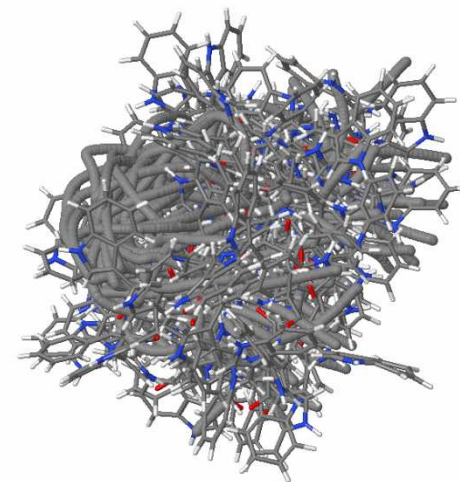
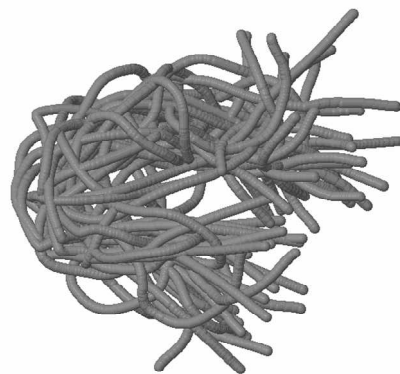
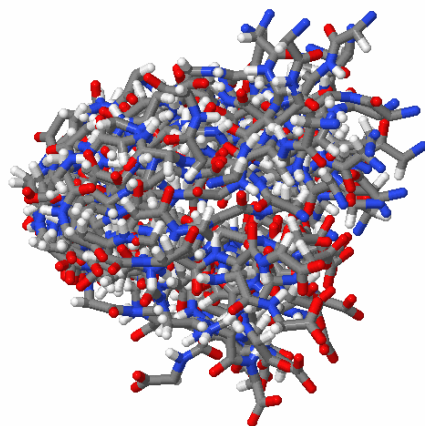
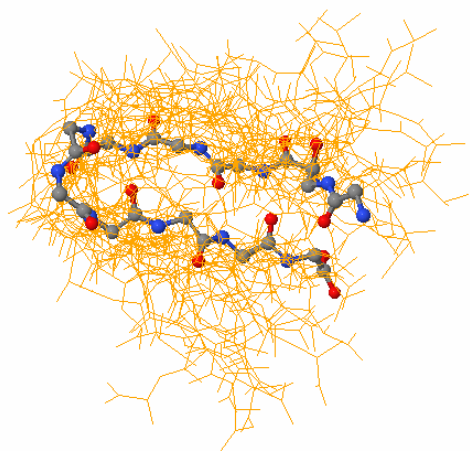
“Folded” (FO, 250851)



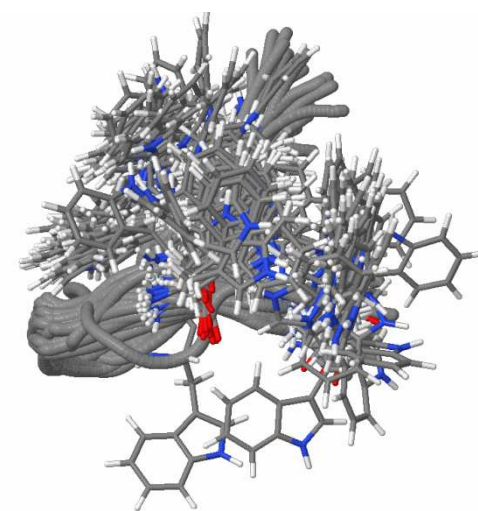
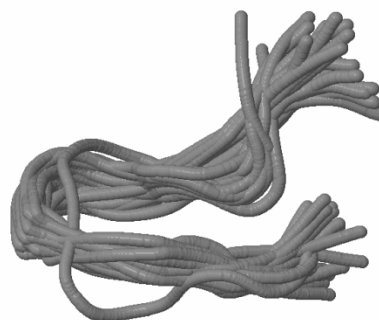
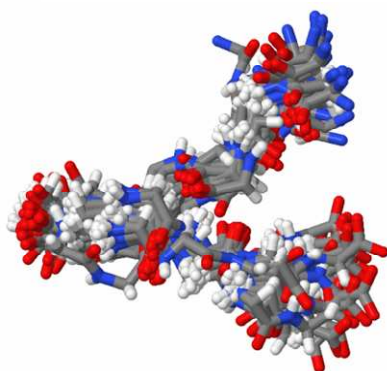
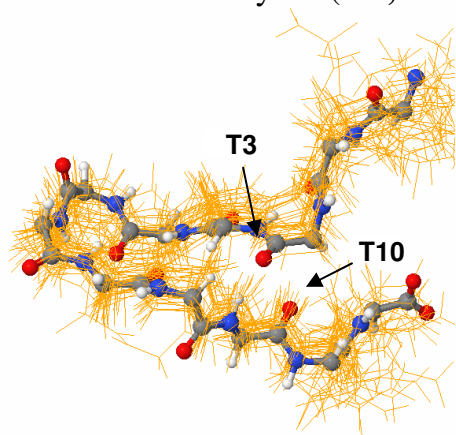
“Bulged” (BT, 214369)



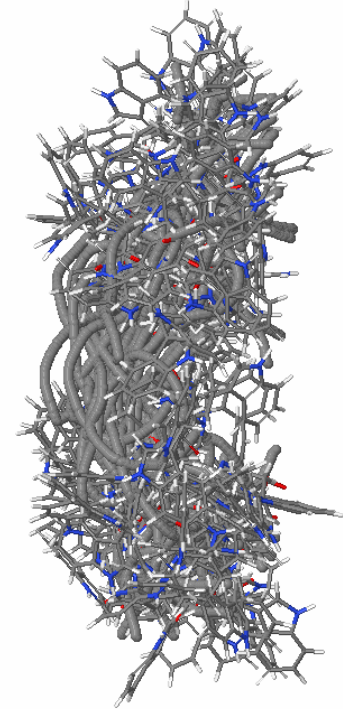
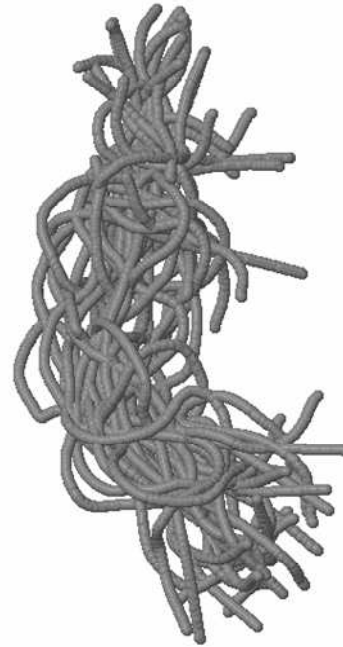
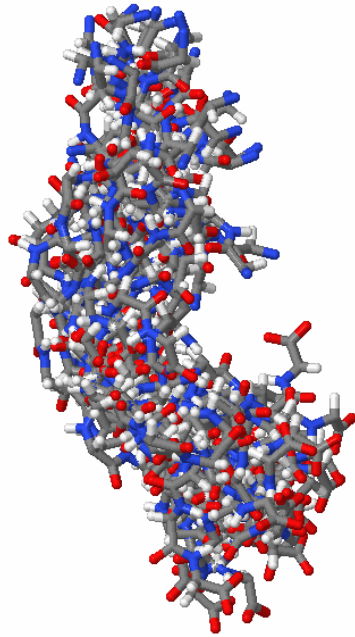
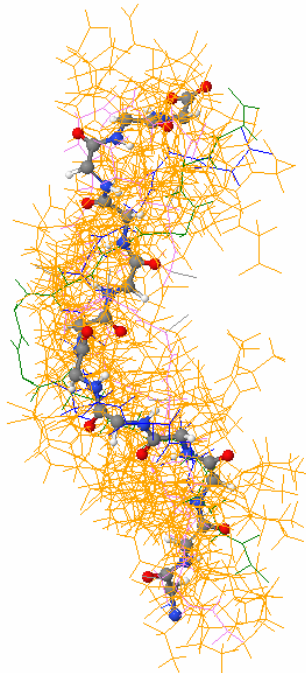
“Disordered” (SR, 271154)



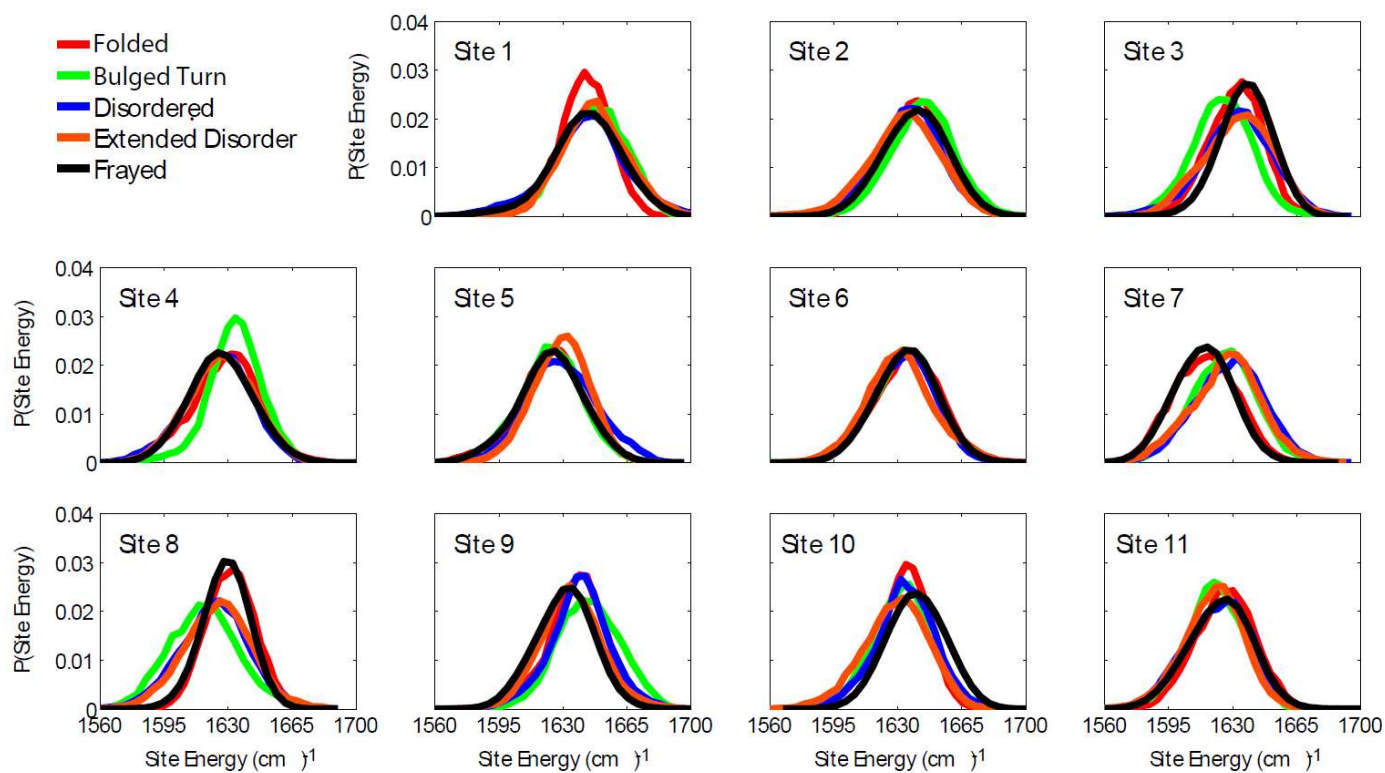
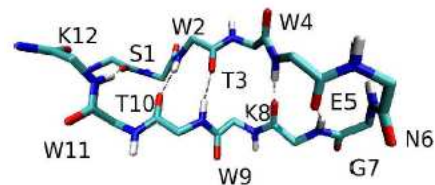
“Frayed” (FR, 11131)



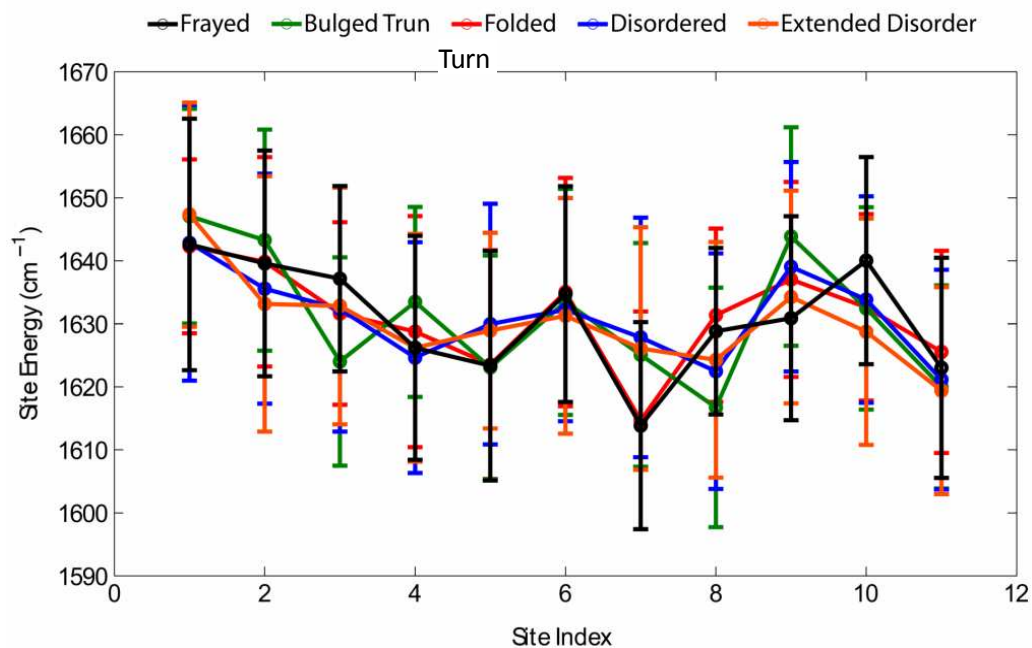
“Extended Disorder” (ED, 64336)



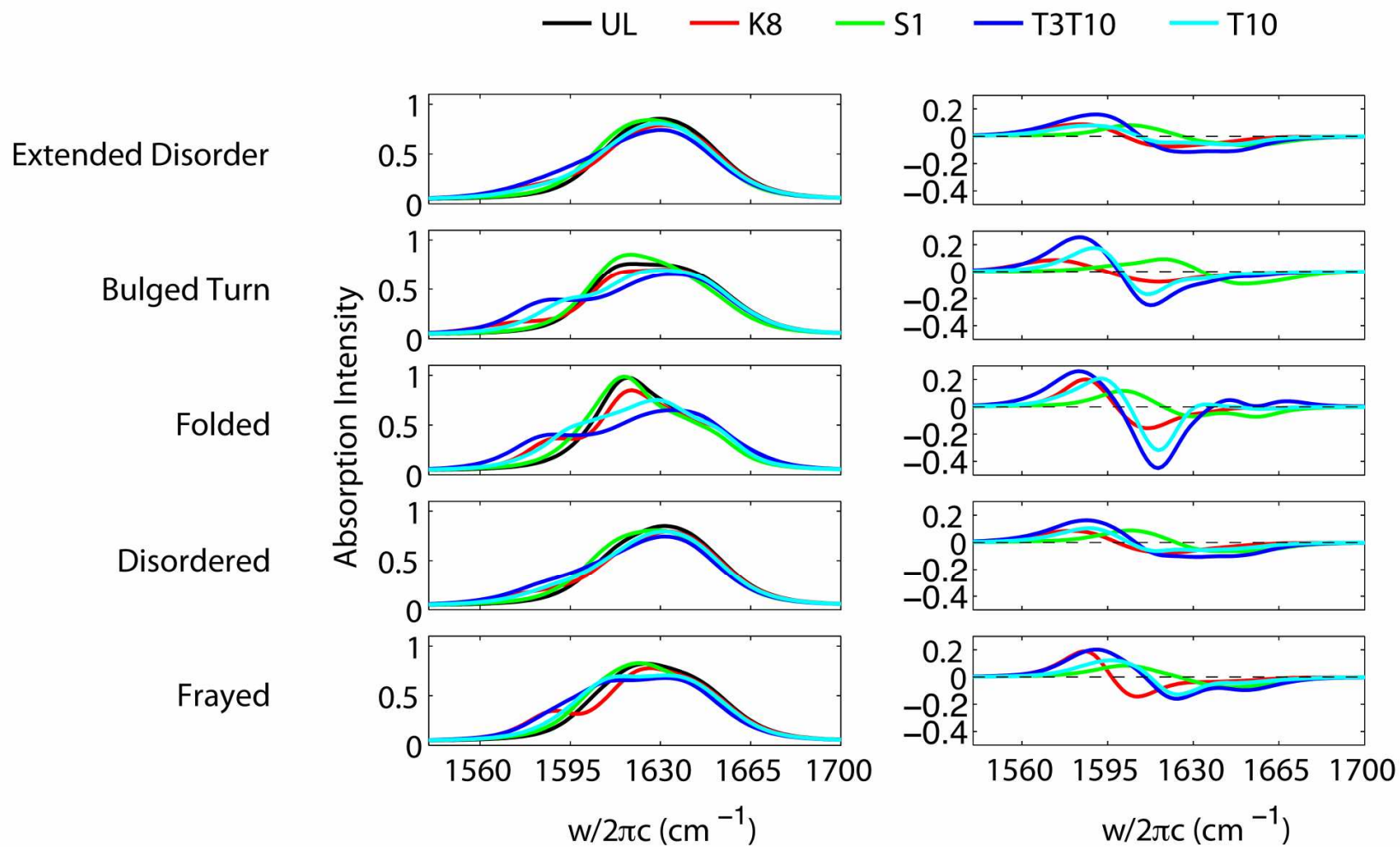
3. Analysis of simulated site energy variation by conformer



Site energy mean values showing error bars with one standard deviation



4. Simulated FTIR and FTIR difference spectra for isotopologues of all Markov States



5. Comparison of spectral features in simulations with experiment.

All units in cm^{-1} .

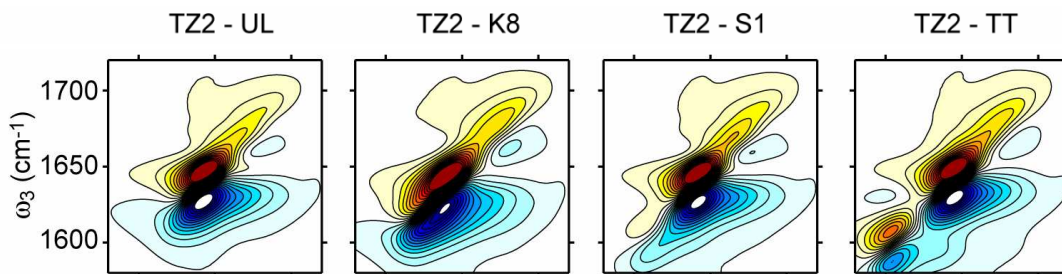
Site	Experiment (25°C)					Experiment (75°C)					Simulations											
	Absorbance Maximum			FWHM [^]		Absorbance Maximum			FWHM		64336 Frayed (FR)			214369 Bulged (BT)			250851 Folded (FO)			271154 Disordered (SR)		
	Ex*	Iso**	Iso2	Iso	Iso2	Ex*	Iso**	Iso2	Iso	Iso2	Peak	Iso	Width	Peak	Iso	Width	Peak	Iso	Width	Peak	Iso	Width
UL	1636					1637					1649			1645			1651			1646		
S1	1633	1629		10		1635					1647	1637	4.6	1660	1647	6.5	1651	1635	5.7	1646	1639	6.8
K8	1635	1598	1615	22	10	1639	1601	1617	17	10	1652	1623	13.7	1644	1608	8.3	1651	1622	5.7	1645	1616	10.8
T 10	1639	1628		9		1644	1632		9		1649	1624	9.8	1653	1628	6.3	1640	1627	3.3	1649	1624	8.3
TT	1635	1603		19		1634	1602		17		1651	1629	13.1	1629	1616	6.6	1645	1622	6.0	1647	1622	10.9

* Excitonic ¹²C band absorbance maximum

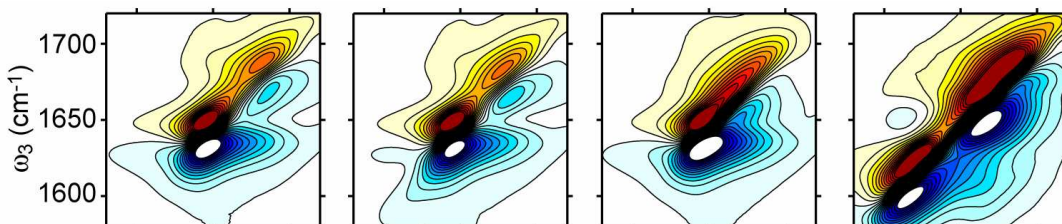
** Isotope shifted peak absorbance maximum

[^] Diagonal peak width (FWHM)

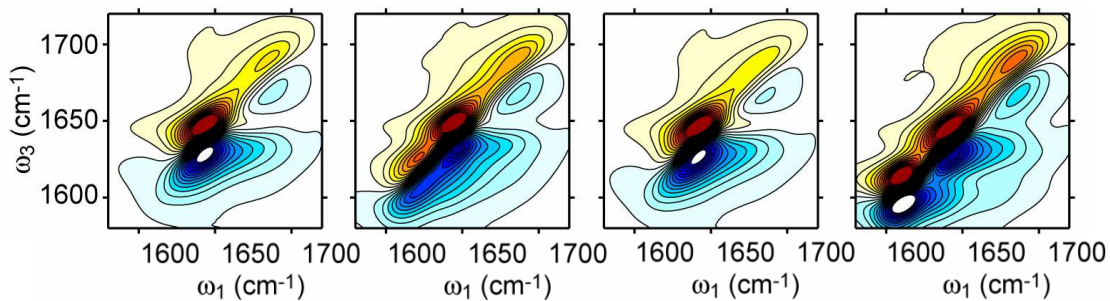
6. 2D IR spectral simulations of TZ2 isotopologues for specific conformations



NL simulation for single structure with intact S1-W12 hydrogen bond.



Slipped registry simulation for a single +1C slipped registry conformer with 4 hydrogen bonds.



Simulations of the 2D IR spectra for the NMR structure of TZ2.