

Supplementary information

Probing the Formation of Isolated Cyclo-FF Peptide Clusters by Far-Infrared Action Spectroscopy

Sjors Bakels^a, Iuliia Stroganova^{b, a} and Anouk M. Rijs*^{b, a}

^a Radboud University, FELIX Laboratory, Institute for Molecules and Materials, Toernooiveld 7, 6525 ED Nijmegen

^b Division of BioAnalytical Chemistry, AIMMS Amsterdam Institute of Molecular and Life Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1108, 1081 HV Amsterdam, The Netherlands

*corresponding author mail: a.m.rijs@vu.nl

Contents

GENERAL	2
1. Mass spectrum	2
2. Nomenclature	3
MONOMER	4
3. Monomer: Infrared 3 μm region	4
4. Monomer: Infrared mid-IR region (1000-1800 cm^{-1} and 3350-3450 cm^{-1}).....	5
5. Monomer: IR-UV hole-burning.....	6
DIMER	7
6. Dimer: Infrared: far-IR comparisons	7
7. Dimer: Infrared mid-IR region (1000-1800 cm^{-1} and 3350-3450 cm^{-1}).....	11
TRIMER	12
8. Trimer: Infrared mid-IR region (1000-1800 cm^{-1} and 3360-3440 cm^{-1}).....	13
TETRAMER	14
9. Tetramer: Infrared mid-IR region (1000-1800 cm^{-1}).....	15
10. Tetramer: N-H wagging	16
OVERVIEW	17
11. Overview	17
12. XYZ files of assigned structures	18

General

1. Mass spectrum

In Fig. SI.1 the mass spectrum of cyclo-FF is presented. This spectrum is taken at a REMPI wavenumber of 37506 cm^{-1} , at which the IR spectra of the higher order clusters ($n > 4$) were obtained. The detection settings (e.g., pusher voltages of the time-of-flight mass spectrometer) were set to detect higher masses, at the expense of the lower masses. The relative intensities are therefore not reflecting their abundances in the molecular beam. At optimal conditions for the monomer (different voltage settings, wavenumber set to 37588 cm^{-1}), its signal was around 1000 times larger than shown in this mass spectrum, while no trimer could be observed. The small peaks with higher masses next to the clusters with $n=3-6$ have a mass of 18, likely due to addition of a water molecule. It is unclear where this originates from.

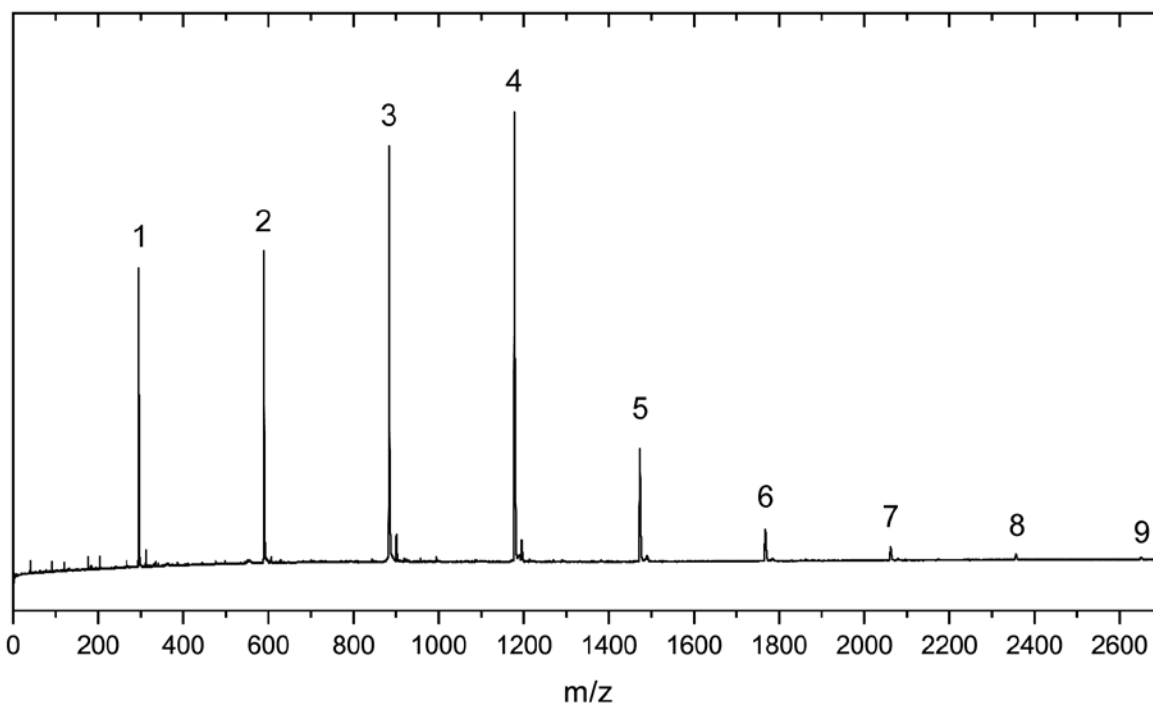


Figure SI.1: Mass spectrum of cyclo-FF, obtained at a REMPI wavenumber of 37506 cm^{-1} and with detection settings optimized for higher order clusters. The number above the peaks indicate the size of the cluster (i.e., number of monomeric units in the cluster).

2. Nomenclature

In this study we will use the nomenclature as commonly used for the monomers of cyclo-FF (e.g. by Zehnacker et al.¹), and extend its use to the aggregates. For monomers the name is derived from the position of the rings: the dihedral angle τ of 60° , -60° or 180° gives a g^+ , g^- or t , respectively. A monomer contains two phenylalanine residues, each containing a phenyl ring. Therefore, each monomer consists of two rings, each with a specific dihedral angle, resulting in conformers such as g^+g^- , g^-t , tt etc. This is graphically shown in Fig. SI.2 for R4 (ring R4) in monomer B.

For dimers an extra factor comes into play, namely the way the two monomers are positioned relative to each other. In the nomenclature, this is indicated by a symbol between the two monomers. This can be either doubly hydrogen bonded such as in the figure (e.g. $g^+g^- = g^+g^-$) or connected by a single hydrogen bond (e.g. $g^+g^- - g^+g^-$), or without hydrogen bonds, so with dispersion or electrostatic interactions ($g^+g^-Xg^+g^-$).

For the double hydrogen bonded dimers there are multiple ways in which they can be connected. For example, in Fig. SI.2 rotation of monomer A by 180° will change the C=O and N-H involved in hydrogen bonding. The order of appearance in notation for the dimer is determined by starting on one of the accepting C=O groups (in the example that is either the C=O at location 1 or 4), then naming the other residue in the monomer (respectively 2 or 3). After that, the other monomer, starting with the donating N-H (so 3 or 2) is added. This can provide two different names for the same molecule, such as $g^+g^- = g^+g^-$ and $g^-g^+ = g^-g^+$. In such cases, we choose the order $g^+ > g^- > t$, resulting in $g^+g^- = g^+g^-$. For trimers and higher order clusters the same nomenclature is used as for the dimer.

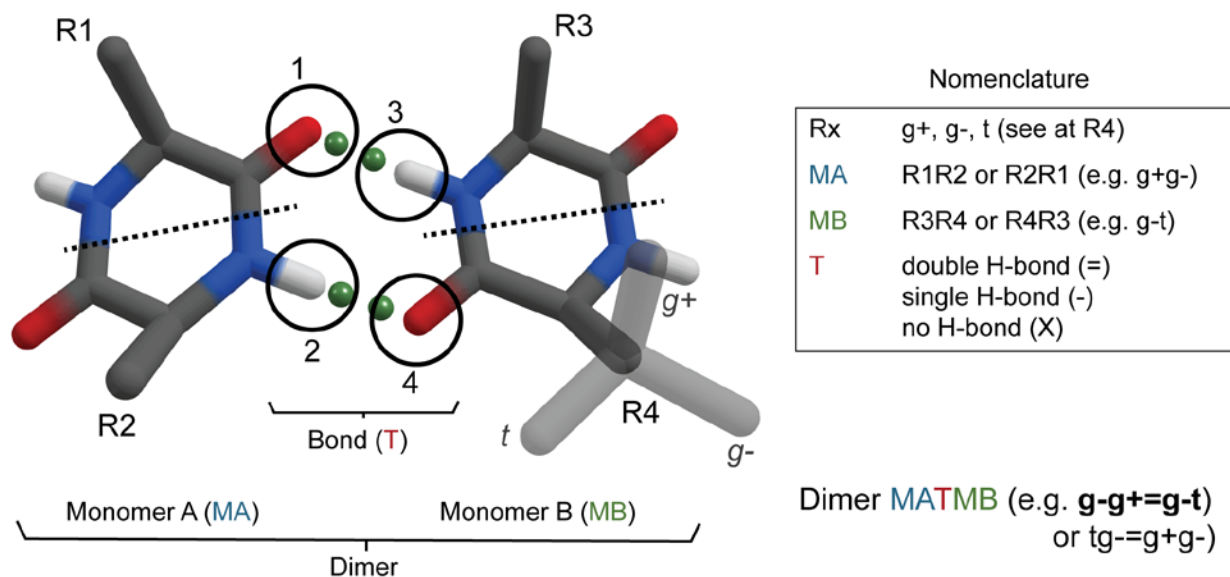


Figure SI.2: Nomenclature as is used throughout this work. The circles with numbers indicate the order of how the name is given (1-2-3-4), this can also be the other way around. Colors: Carbon (dark grey), nitrogen (blue), oxygen (red), hydrogen (light grey). The aromatic rings are not shown in this figure for clarity reasons. On the right bottom the way the name of a dimer is built up is shown.

¹ A. Perez-Mellor, I. Alata, V. Lepere and A. Zehnacker, *J. Mol. Spectrosc.*, 2018, **349**, 71-84.

Monomer

3. Monomer: Infrared 3 μm region

A comparison with the previous results by Zehnacker et al.¹ was done by remeasuring the 3 μm region (3340-3440 cm^{-1}), and performing anharmonic calculations at the B3LYP-D3/jun-cc-pVDZ level of theory (see Fig. SI.3). The anharmonic bands are manually shifted by +21 wavenumbers to match the experimental data. The experimental peak positions at 3402, 3416 and 3425 cm^{-1} are shifted with respect to the results of Zehnacker et al. by +9 cm^{-1} , which is most probably a result of calibration. The main difference between the two spectra is in the relative intensities between the 3402 peak and the other two. In the work of Zehnacker et al., the two smaller bands have a higher relative intensity than the two peaks in this work. One possible explanation is that in the former saturation has taken place, also because of the broader peaks.

Zehnacker et al. assigned the strong band (3402) to the N-H stretch of the g- moiety, the third band (3425) to the N-H stretch of the g+ moiety, and the middle band (3416) to a combination band of the C=O stretch and N-H bend vibrations. The calculations we performed, both harmonic (SI.4) and anharmonic, show only evidence for assignment of the second peak to the N-H stretch of the g+ moiety, and the third to overtones.

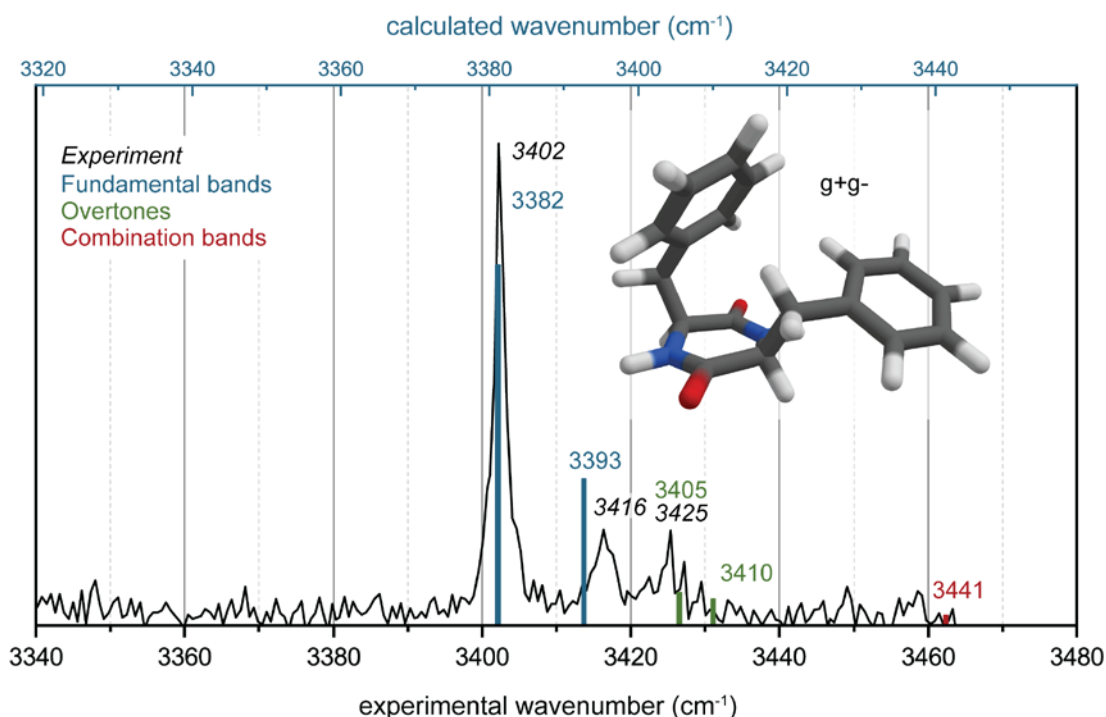


Figure SI.3: Experimental (black) and calculated (colored) anharmonic IR spectra of the g+g- structure. The corresponding structure is shown in the inset. The bottom x-axis contains the experimentally obtained values after calibration. The top x-axis, calculated wavenumber, is the x-axis of the calculations, and is shifted to match the experiment.

¹ A. Perez-Mellor, I. Alata, V. Lepere and A. Zehnacker, *J. Mol. Spectrosc.*, 2018, **349**, 71-84.

4. Monomer: Infrared mid-IR region (1000-1800 cm^{-1} and 3350-3450 cm^{-1})

In Fig. SI.4 the infrared spectra of the monomer of cyclo-FF is shown in the region of 1000 to 1800 cm^{-1} (left panel). The experimental spectrum (black, top) contains a single intense peak at 1718 cm^{-1} , two peaks equal in intensity at 1411 and 1436 cm^{-1} with a smaller peak at 1458 cm^{-1} , a double peak at 1321 and 1342 cm^{-1} , and some minor features throughout the rest of the spectrum. The calculated spectra (B3LYP-D3/6-311+G(d,p), scaled by 0.976) of the six conformers all show a similar pattern: A dominant peak around 1700 cm^{-1} (containing both C=O oscillators), a clear peak around 1400 cm^{-1} , and some smaller features to the blue side of the spectrum. Only the region between 1200 and 1350 cm^{-1} varies between the different calculated spectra. However, the similar spectral features above 1350 cm^{-1} and insufficient specificity below 1350 cm^{-1} makes assignments based solely on the mid-IR inconclusive.

The experimental and calculated spectra in the free N-H stretching region between 3350 and 3450 cm^{-1} are presented in the right panel of Fig. SI.4. Since the far-IR region makes for a very confident assignment to the g+g- structure, the calculated spectra here are scaled by 0.954 in order to match the experiment. The two fundamental bands of the anharmonic calculation in Fig. SI.3 agree with the scaled harmonic bands of g+g- in Fig. SI.4. This scaling factor is also used for comparison with the higher order clusters (Fig. SI.7 for the dimer, Fig. SI.8 for the trimer).

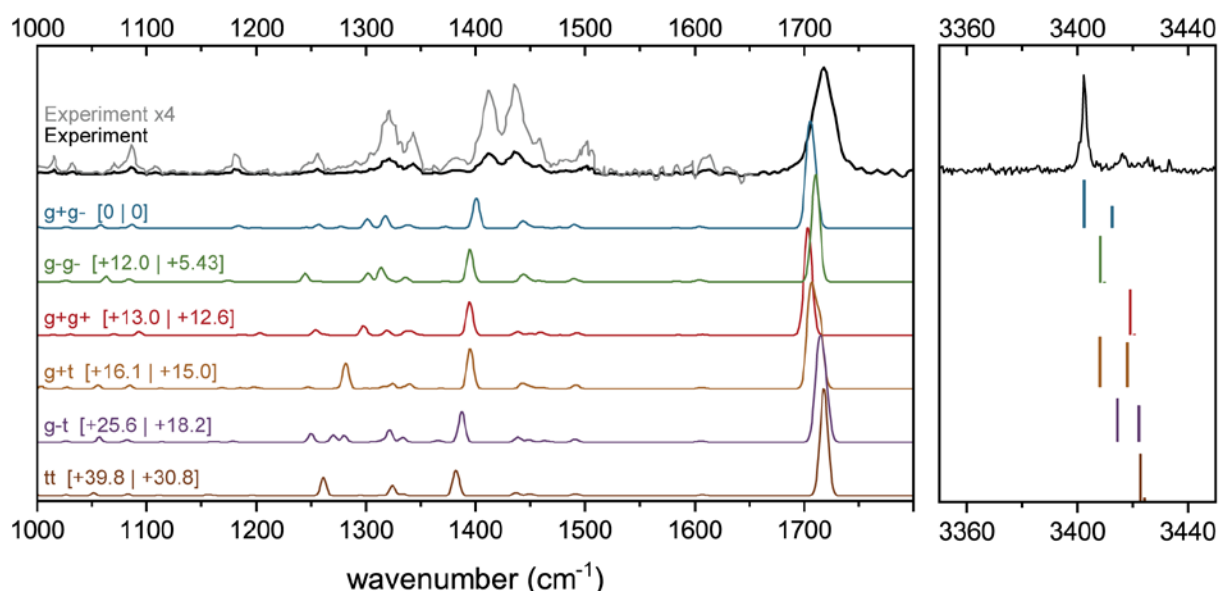


Figure SI.4: Left panel: Experimental (black, top) and calculated (colored) IR spectra of the six possible monomeric structures, arranged from lowest energy to highest (top to bottom). Calculated spectra are scaled by 0.976, calculations have been done at the B3LYP-D3/6-311+G(d,p) level. Right panel: amide A or (free) N-H stretching region. Calculated spectra are scaled by 0.954 to match the experimental spectrum.

5. Monomer: IR-UV hole-burning

In Fig. SI.5a the IR-UV hole-burning spectrum of the monomer of cyclo-FF is shown, with the IR laser put at a wavenumber of 3402 cm^{-1} . According to the calculations in Fig. SI.4, this wavenumber is only observed in the $g+g-$ conformer, and it is therefore “safe” to use here. A depletion of around 60 % can be observed in virtually all peaks in the spectrum, except for a peak at 38146 cm^{-1} and 37612 cm^{-1} (the latter one indicated with a red arrow). In Fig. SI.5b the IR spectrum taken at 37612 cm^{-1} (conformer b) is shown, together with the $3\text{ }\mu\text{m}$ spectrum of the major conformer (conformer a) and the calculated spectra of the monomer. A comparison yields the assignment of conformer b to the second lowest energy structure, $g-g-$.

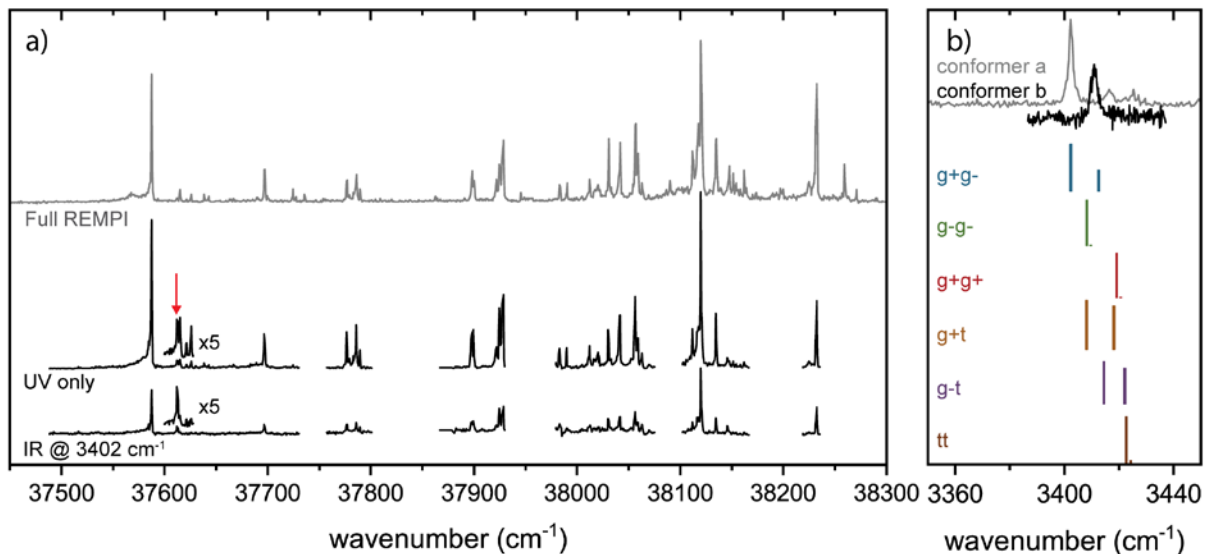


Figure SI.5 a) IR-UV hole-burning spectrum of the cyclo-FF monomer. Top spectrum (grey) is a REMPI spectrum taken at an earlier stage and is used as reference. The other spectra are taken simultaneously in an on/off fashion, the middle spectrum with only the UV laser, and the bottom spectrum with both UV and IR laser. The IR laser is put at the obtained wavenumber 3402 cm^{-1} as is shown in Fig. SI.3. b) OPO spectra obtained from both the main conformer a (in grey) and by putting the REMPI laser at 37612 cm^{-1} (black, conformer b), together with the calculated spectra of the monomer (colored stick spectra), scaled by 0.954.

Dimer

6. Dimer: Infrared: far-IR comparisons

The following 4 figures contain 22 unique lowest energy structures, and 2 structures with no hydrogen bonding, along with their calculated spectra.

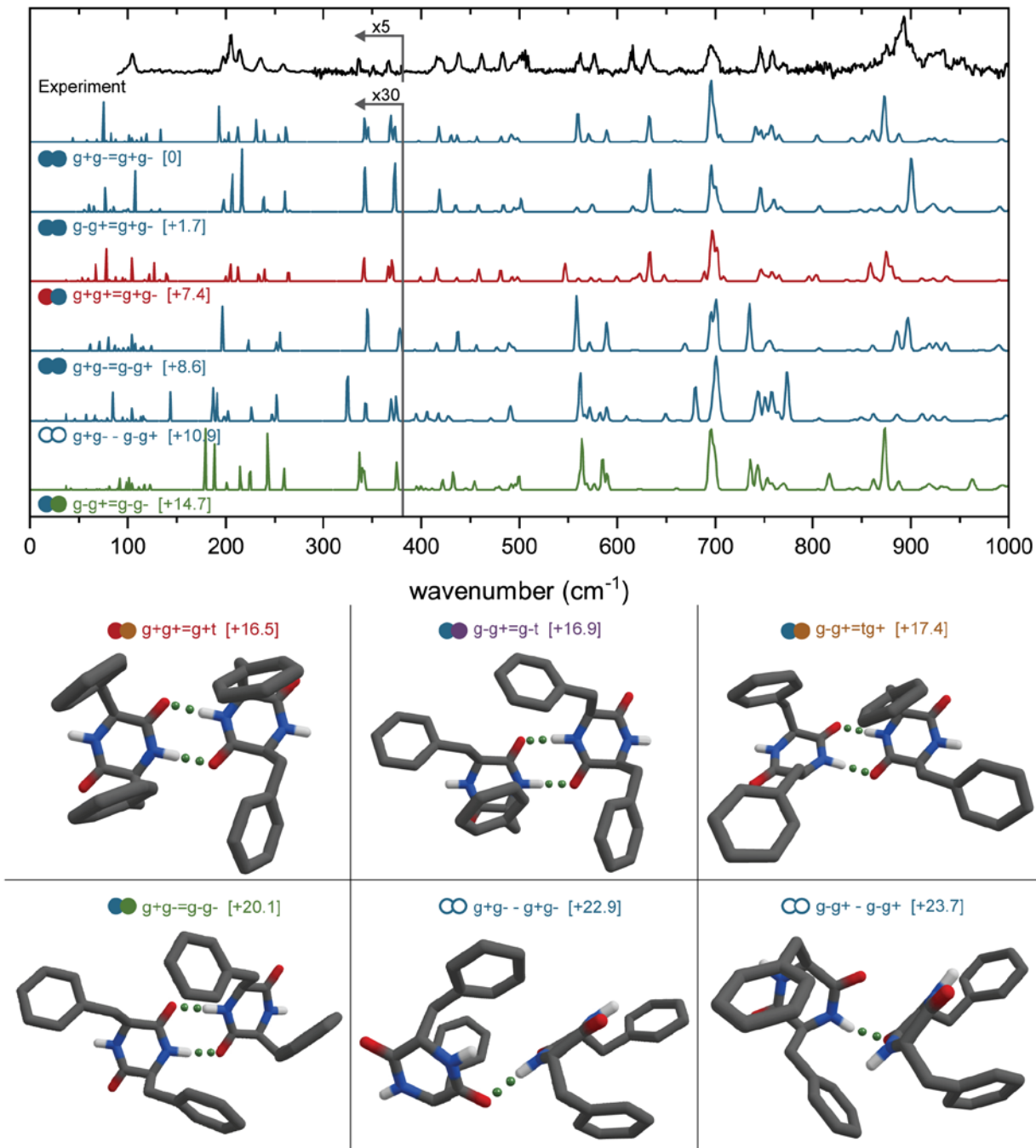
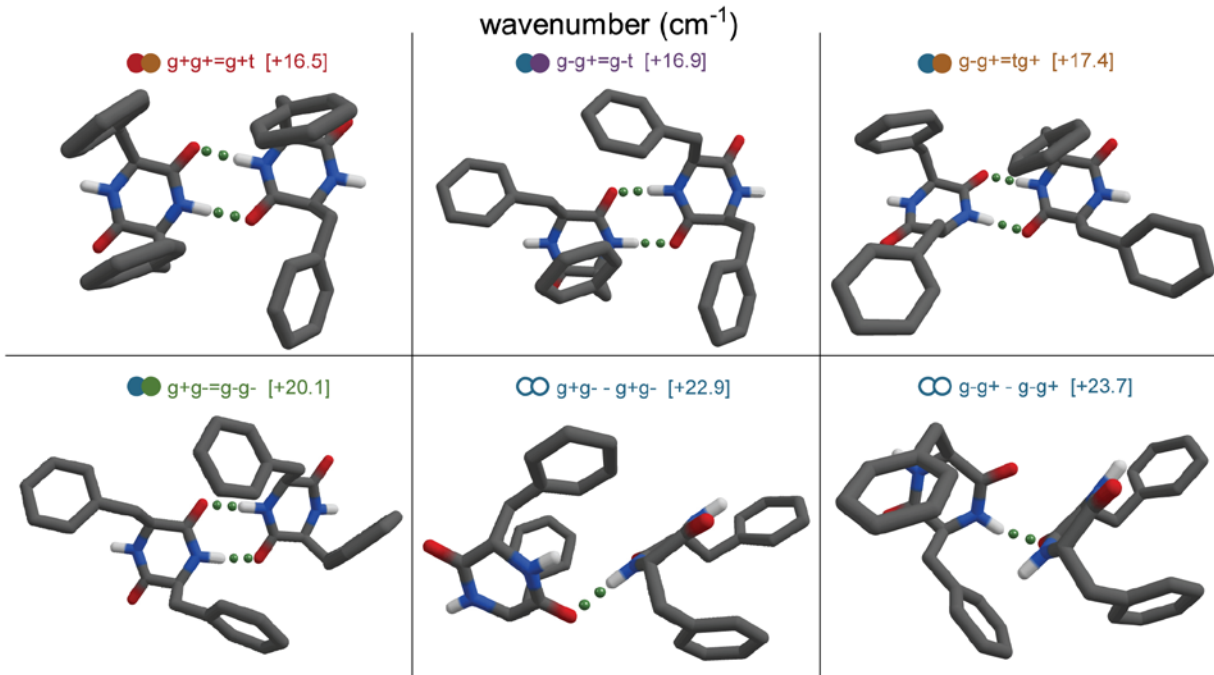
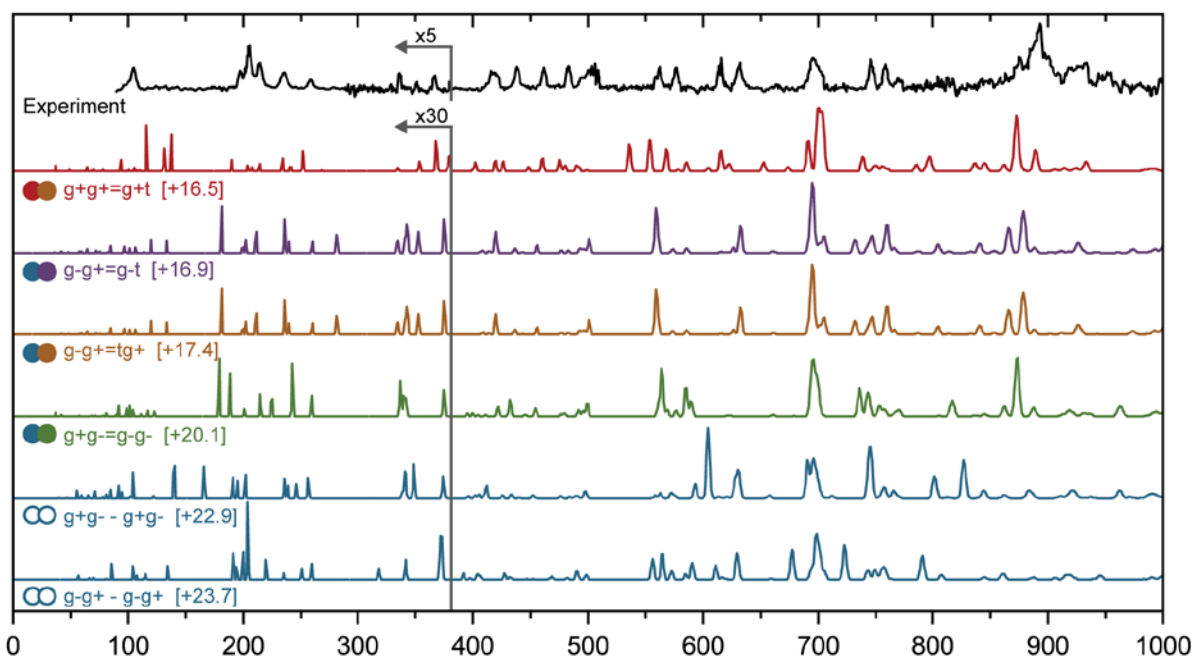
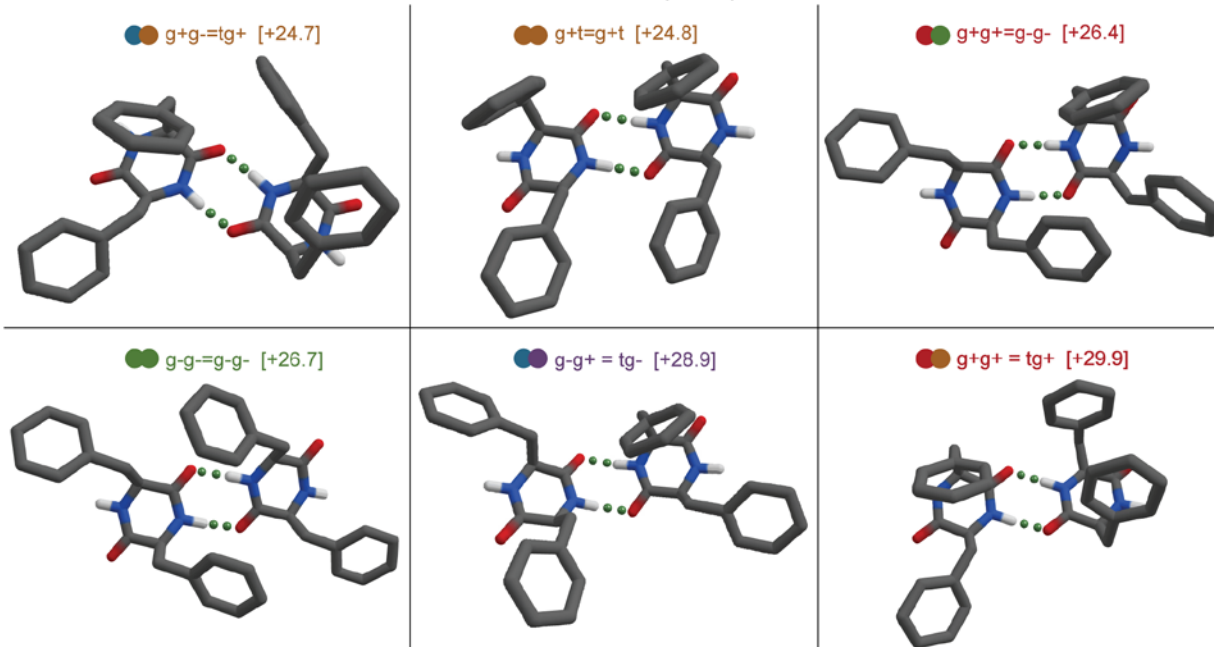
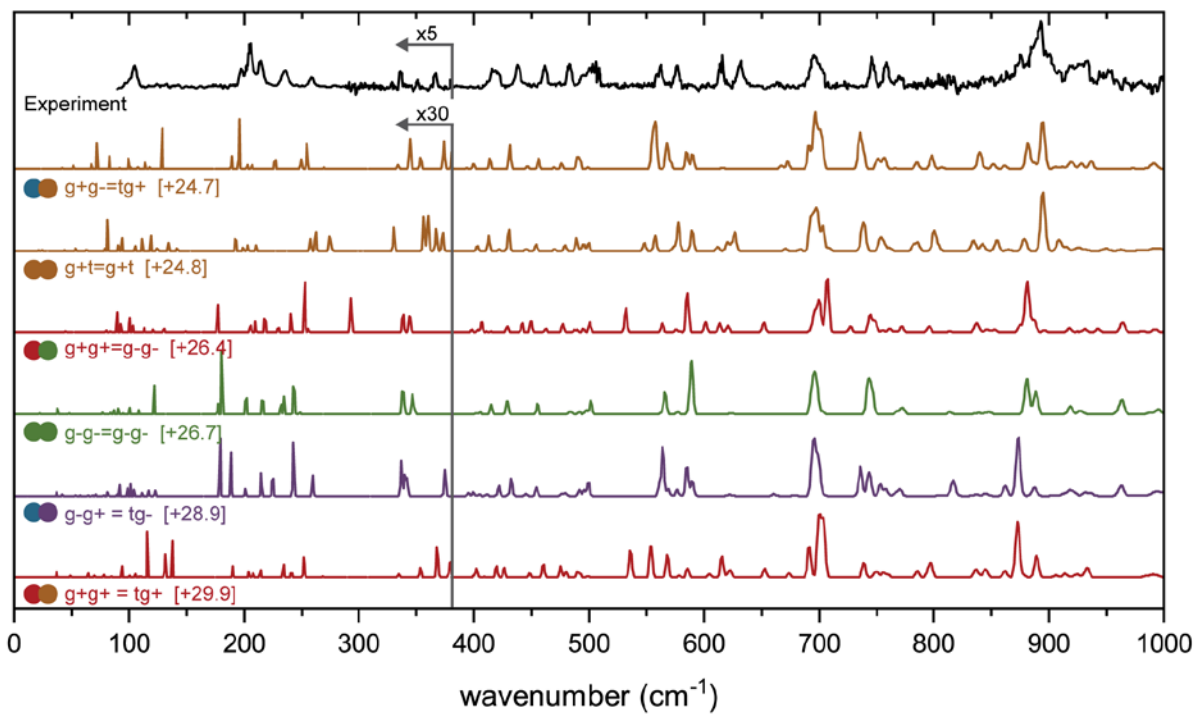
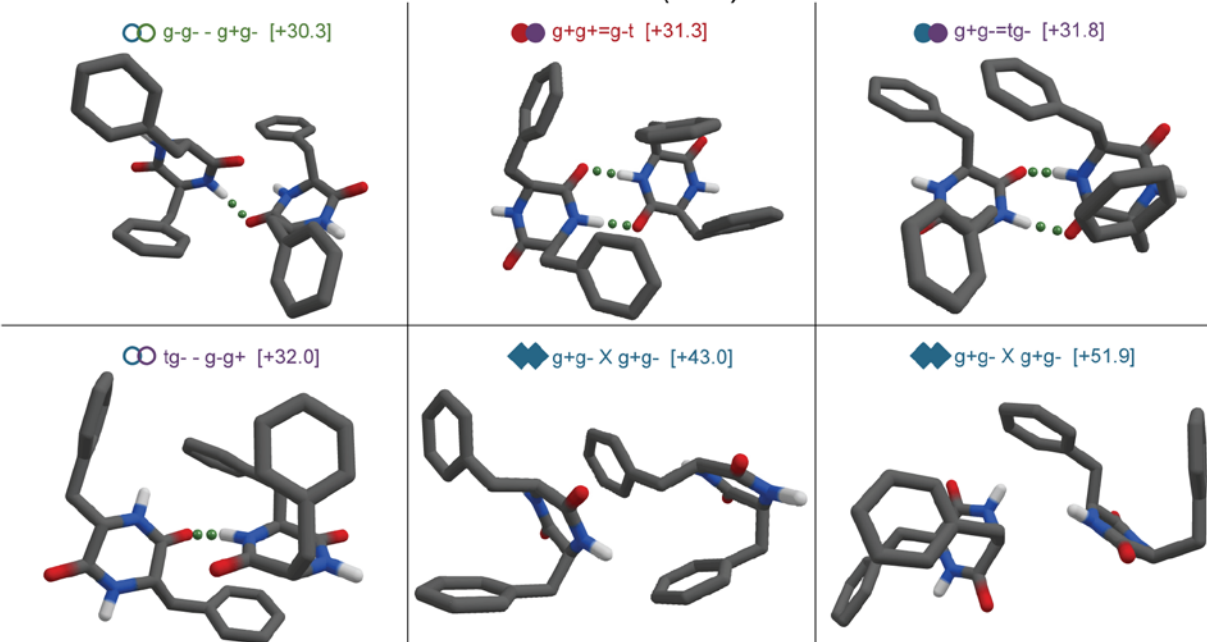
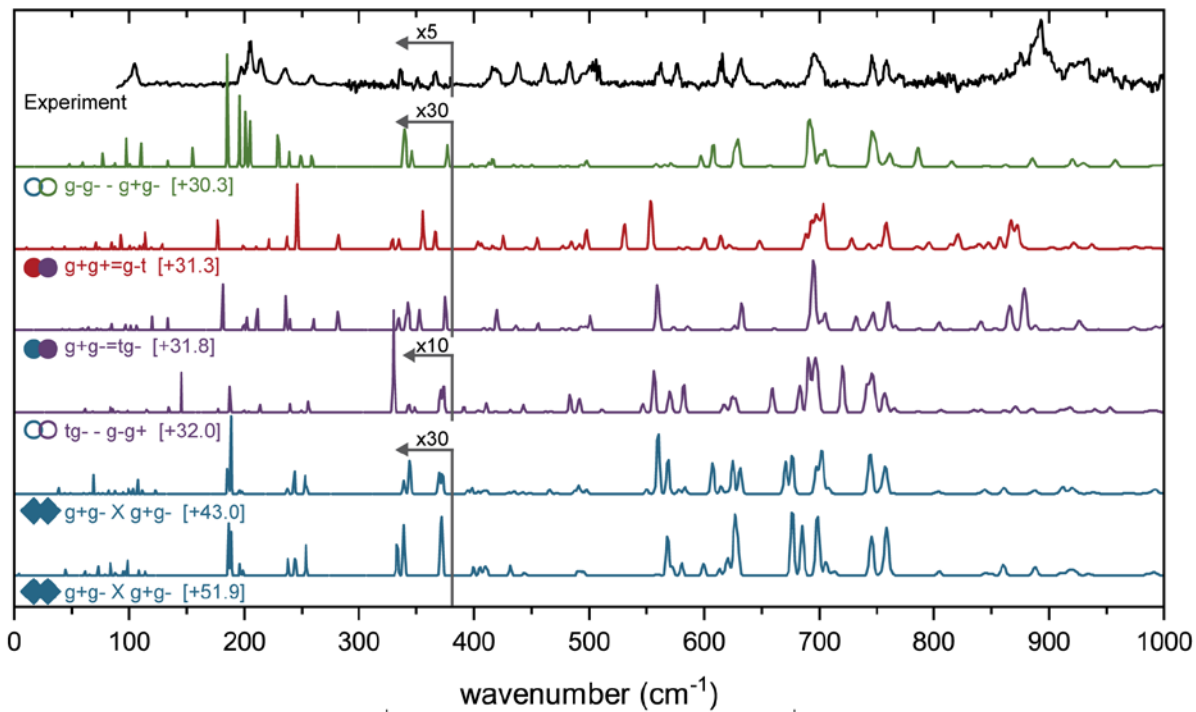


Figure S1.6: Experimental (black, top) and calculated (colored) far-IR spectra of six possible dimer structures, arranged from lowest energy to highest (top to bottom). The corresponding structures are shown at the bottom of the figure. The spectra below 380 cm^{-1} are multiplied by 30 for clarity. All calculated spectra are scaled by 0.976, calculations have been done at the B3LYP-D3/6-311+G(d,p) level. Colors in front of the names indicate which monomers are part of the dimer. Closed rings indicate double-hydrogen bonded systems, open rings singly-hydrogen bonded, and triangles non-hydrogen bonded.







7. Dimer: Infrared mid-IR region ($1000\text{-}1800\text{ cm}^{-1}$ and $3350\text{-}3450\text{ cm}^{-1}$)

The experimental spectrum of the dimer in the mid-IR region is, together with the three most promising calculated spectra, presented in Fig. SI.7 ($1000\text{-}1800\text{ cm}^{-1}$ in the left panel, $3350\text{-}3450\text{ cm}^{-1}$ in the right panel). The first region does not show any significant differences between the three calculations: all show a matching double peak around 1700 cm^{-1} , and a too much redshifted peak around 1425 cm^{-1} . The $3\text{ }\mu\text{m}$ region however shows clear differences. Calculations are there scaled according to the monomer, by 0.954. The asymmetric $g+g=g+g-$ conformer (blue), contains two almost equally large bands (3403 cm^{-1} peak arising from the free N-H from the $g-$ side, 3416 cm^{-1} from the $g+$ side). The peak at 3403 cm^{-1} is located at the same position as the experimental peak. The second peak is however not observed in the experiment, although some small intensity can be observed, which is, as a result of its low intensity, more likely to arise from overtones such as observed in the spectrum of the monomer. The other two dimers have C_2 symmetry and show therefore only 1 peak, either around 3404 cm^{-1} (free $g-$, so $g-g+=g+g-$), or around 3415 cm^{-1} (free $g+$, so $g+g-=g-g+$). The spectrum of $g-g+=g+g-$ consequently overlaps the best with the experiment, as was also concluded from the far-IR.

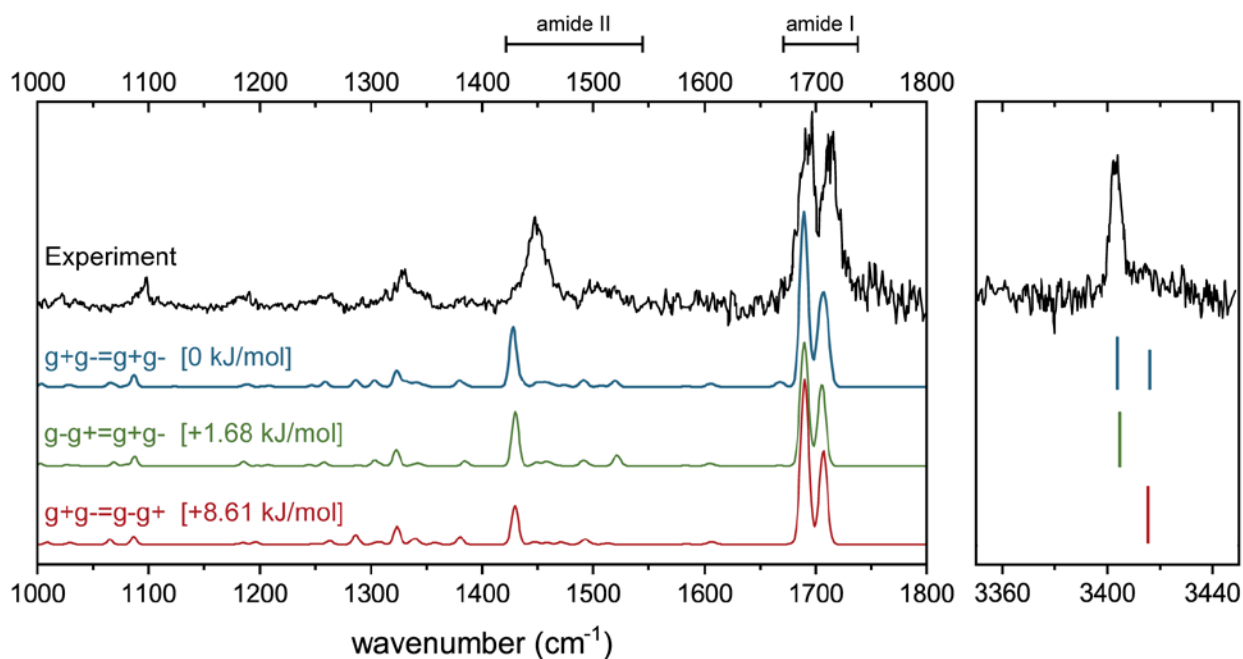


Figure SI.7: Experimental (black, top) and calculated (colored) far-IR spectra of the three lowest energy structures of the dimer containing only $g+g-$ subunits, arranged from lowest energy to highest (top to bottom) for the mid-IR (left panel) and the $3\text{ }\mu\text{m}$ (amide A) region. The calculated spectra are scaled by 0.976 (mid-IR) and 0.954 ($3\text{ }\mu\text{m}$ region), all calculations have been done at the B3LYP-D3/6-311+G(d,p) level of theory. The amide I and II bands are indicated above the figure.

Trimer

Table SI.1: Relative energies, both zero-point energy corrected and Gibbs free energy at 300 K, for the calculated trimer conformers. Calculations are performed at the B3LYP-D3/6-311+G(d) level of theory. All the units are in kJ/mol.

Structure	ZPE (kJ/mol)	Gibbs free energy (300 K, kJ/mol)
<i>g+g-=g+g-=g+g-</i>	0	0
<i>g-g+=g+g-=g+g-</i>	2.11	1.18
<i>g+g-=g+g-Xg+g-_1</i>	6.91	7.14
<i>g+g-=g+g-=g-g+</i>	9.29	11.7
<i>g+g-=g-g+=g+g-</i>	11.1	13.1
<i>g-g+=g+g-Xg+g-_1</i>	15.0	9.60
<i>g-g+=g+g-=g-g-</i>	22.3	17.3
<i>g-g+=g+g-Xg+g-_2</i>	35.1	34.8
<i>g+g-=g+g-Xg+g-_2</i>	36.5	43.4

8. Trimer: Infrared mid-IR region ($1000\text{-}1800\text{ cm}^{-1}$ and $3360\text{-}3440\text{ cm}^{-1}$)

The mid-IR experimental spectrum (top trace in left panel of Fig. SI.8), shows a few broader features below 1400 cm^{-1} , a large band around 1450 cm^{-1} in the amide II region, and two peaks at 1691 cm^{-1} and 1713 cm^{-1} in the amide I region. The six calculations (as presented in Fig. 4 in the main text) all show matching intensities around the peaks below 1400 cm^{-1} , but predict the amide II bands too much to the red side of the spectrum (-20 cm^{-1}), similar as in the calculations for the monomer and dimer. Both structures that are built up of a dimer and a non-hydrogen bonded monomer have an additional peak around 1415 cm^{-1} , which is not observed in the experimental spectrum. The amide I region shows a double peak for all conformers, however for the latter two structures the intensities of both peaks are the opposite of what is observed in the experiment.

In the right panel of Fig. SI.8 the experimental and calculated spectra in the $3\text{ }\mu\text{m}$ region (amide A, free N-H stretching) are presented. Here, the calculated spectra are scaled by 0.954 as was determined for the monomer. Two peaks are expected in this region for the first 4 (3,0) conformers (because they have 2 free g- groups on the outside and no C_2 symmetry), and four are expected for the (2,1) conformers, with 4 free N-H groups. Similar as the dimer, with two g- groups on the outside, two close lying peaks (since similar environment, but not completely symmetric) are predicted around 3406 cm^{-1} , while two free g+ groups give two closely lying peaks around 3416 cm^{-1} . These two options are the g-g+=g+g-=g+g- (free g- groups) and g+g=g+g-=g-g+ (free g+ groups) conformers. The g+g-=g+g-=g+g- and g+g=g-g+=g+g- conformers both have 1 g+ and 1 g- group on the outside, which give rise to two peaks, similar in intensity, around 3406 and 3416 cm^{-1} . The experimental spectrum shows two closely lying peaks around 3402 and 3404 cm^{-1} , which points to the assignment of the g-g+=g+g-=g+g- conformer.

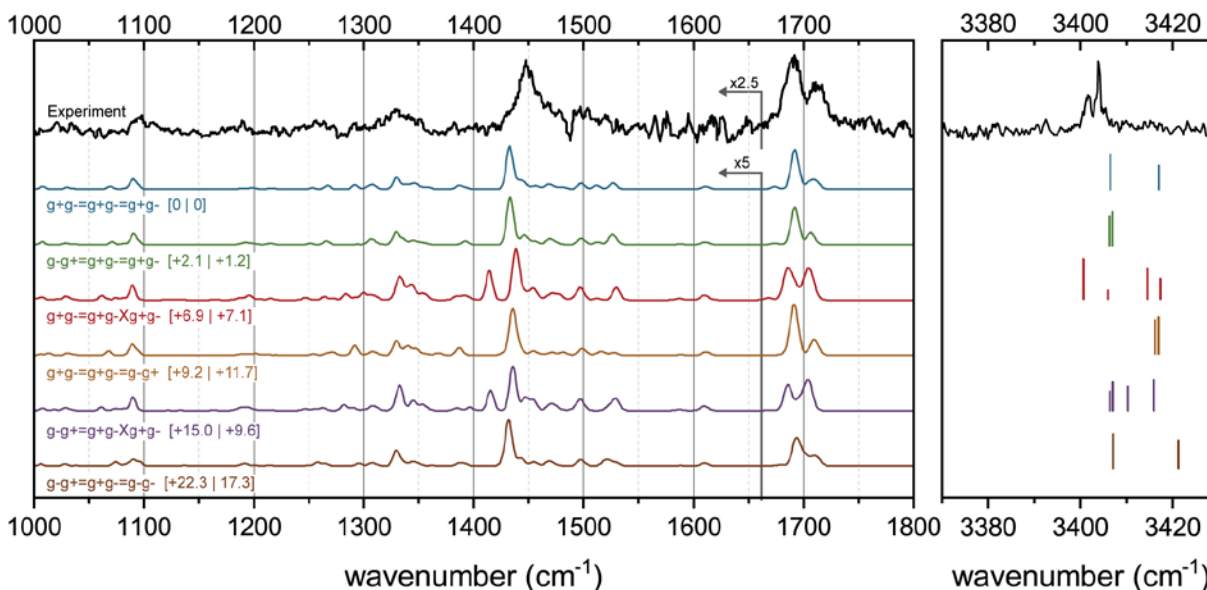


Figure SI.8: Left panel: Experimental (black, top) and calculated (colored) IR spectra of the six possible trimer conformers, arranged from lowest energy to highest (top to bottom). All calculated spectra are scaled by 0.976, calculations have been done at the B3LYP-D3/6-311+G(d) level. For clarity, the spectra below 1655 cm^{-1} are multiplied by 10 (for the calculated spectra), or by 2.5 (for the experimental spectrum). Right panel: amide A region, with the free N-H stretch vibrations. Here, the calculated spectra are presented as stick spectra, and are scaled by 0.954.

Tetramer

Table SI.2: Relative energies, both zero-point energy corrected and Gibbs energy at 300 K, for the calculated tetramer conformers. Calculations are performed at the B3LYP-D3/6-31+G(d) level. All the units are in kJ/mol. The X in the names marks where there is no bond, and the structure consists of 2 separate ladders.

Structure	ZPE (kJ/mol)	Gibbs free energy (300 K, kJ/mol)
<i>g+g-=g+g-Xg+g-=g+g-_1</i>	0.00	0.00
<i>g+g-=g+g-Xg-g+=g+g-_1</i>	9.33	6.20
<i>g+g-=g+g-Xg-g+=g+g-_2</i>	10.9	0.92
<i>g+g-=g+g-Xg+g-=g+g-_2</i>	11.6	11.4
<i>g-g+=g+g-Xg-g+=g+g-_1</i>	19.1	5.63
<i>g+g-=g+g-=g+g-=g+g-</i>	27.4	15.3
<i>g-g+=g-g+=g+g-=g+g-</i>	29.4	18.0
<i>g-g+=g+g-Xg-g+=g+g-_2</i>	47.1	45.1
<i>g-g+=g+g-=g+g-Xg+g-_1</i>	53.1	36.6
<i>g-g+=g+g-=g+g-Xg+g-_2</i>	55.2	51.2

9. Tetramer: Infrared mid-IR region ($1000\text{-}1800\text{ cm}^{-1}$)

The tetramer IR spectrum, taken at a REMPI wavenumber of 37506 cm^{-1} , is presented in Fig. SI.9 for the mid-IR region. Calculations (colored spectra in the figures) are performed at the B3LYP-D3/6-31+G(d) level of theory. Two structures (green in the figures, $g+g-=g+g-=g+g-=g+g-$ and $g-g+=g-g+=g+g-=g+g-$) consists of a single ladder (4,0 with $n=4$), double hydrogen bonded, and is built up of the main trimer conformer. The others are either 2 ladders of $n=2$ (2,2), or a ladder of $n=3$ and a monomer (red, 3,1).

The mid-IR spectrum (Fig. SI.9) shows a strong feature in the amide I region at 1684 cm^{-1} , and a minor feature around 1714 cm^{-1} . It is best reproduced by the three lowest (2,2) energy structures. The amide II peak around 1450 cm^{-1} is predicted well by most calculations, in contradiction to the other clusters, where we found this calculated peak consequently too much redshifted. The remaining part of the mid-IR doesn't show much features except for a slight blob above 1300 cm^{-1} , which is predicted by all calculations.

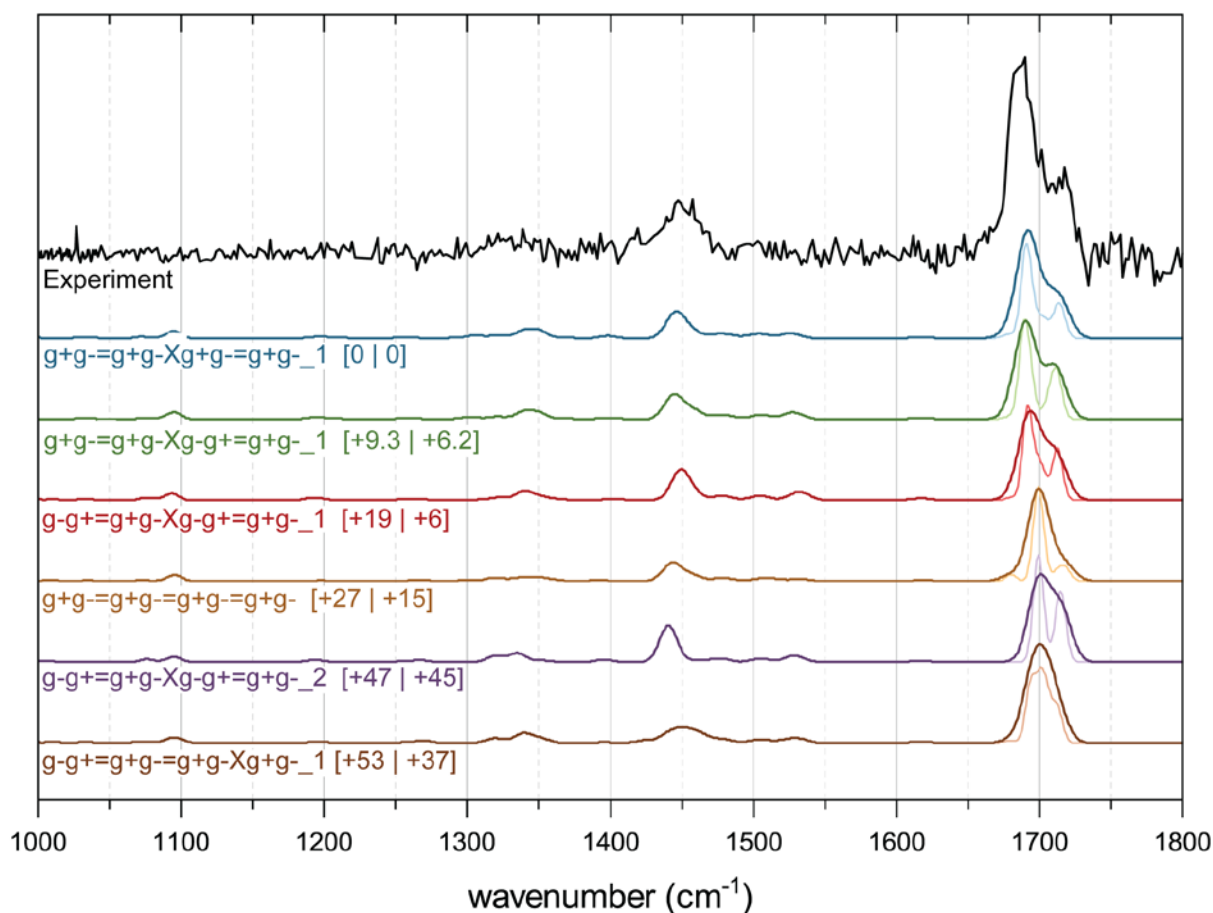


Figure SI.9: Experimental (black, top) and calculated (colored) mid-IR spectra of the six possible tetramer conformers, arranged from lowest energy to highest (top to bottom). All calculated spectra are scaled by 0.976, and convoluted at 1% (0.5% in the amide I, light colors) of the wavenumber. Calculations have been performed at the B3LYP-D3/6-31+G(d) level. Zero-point corrected energies (left), and Gibbs free energies are given between brackets in kJ/mol.

10. Tetramer: N-H wagging

In Fig. SI.10 two plots are presented, both showing wavenumbers versus intensity of calculated vibrations of the monomer, dimer, trimer and tetramer. The vibrations in both Fig. SI.10a and SI.10b are divided into groups, with different colors and symbols to show their origin. In Fig. SI.10a free N-H wagging motions are plotted. Here, blue represents the g^+ N-H groups, while red represents the g^- N-H groups. Symmetric or anti-symmetric motions of 2 g^+ or g^- N-H groups are color coded with blue and red, respectively. The purple color is used for motions involving both a g^+ and a g^- group. Evidently, specific regions within the spectrum can be assigned to these specific vibrations. For example, the region between 520 and 600 cm^{-1} is predominantly occupied by g^+ motions, although some g^- and g^+g^- motions are also present. The region between 625 and 645 cm^{-1} however, contains solely vibrations of g^- N-H groups. This leads to the assignment of the experimental peak at 633 cm^{-1} to free g^- N-H wagging motions. The high intense purple dots around 680 cm^{-1} are a result of monomer g^+g^- motions, and the absence of a peak here in the experimental spectrum suggests that no monomer is present in the tetramer (it makes the presence of the high energy 3,1 structures unlikely).

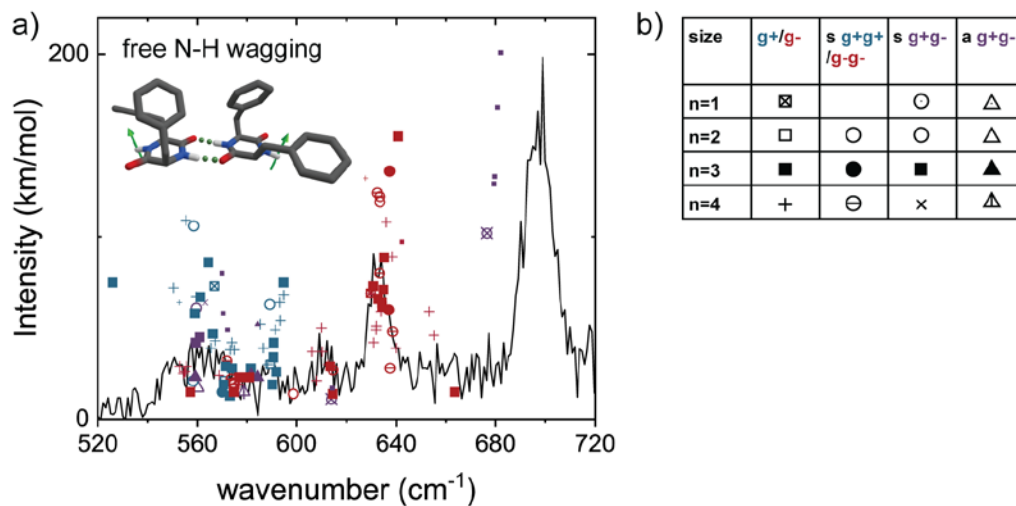


Figure SI.10: Positions of calculated vibrations versus their intensity for the free N-H wagging modes between 520 and 690 cm^{-1} , with in b) the legend. The experimental spectrum of the tetramer is shown in the background (with normalized intensity). The inset in a) shows an example of the vibrations: $s\ g^-g^-$ (so red open circle). Smaller symbols indicate that the origin of this vibration is a monomer unit within a cluster (so for example (3,1) tetramer). Note: Here, the nomenclature such as g^+g^+ means something else than the molecule g^+g^+ .

Overview

11. Overview

In Fig. SI.11 an overview is given of all assigned spectra and corresponding structures. The width of the calculated spectra is taken as 1% of the wavenumber, which matches the characteristics of the IR laser. However, depending on the specific settings on the day of measurement this can be better or worse. For example, the experimental peaks around 1700 cm^{-1} had in reality a better resolution than this 1%, as a result of which the double peak is not visible in the calculated spectra.

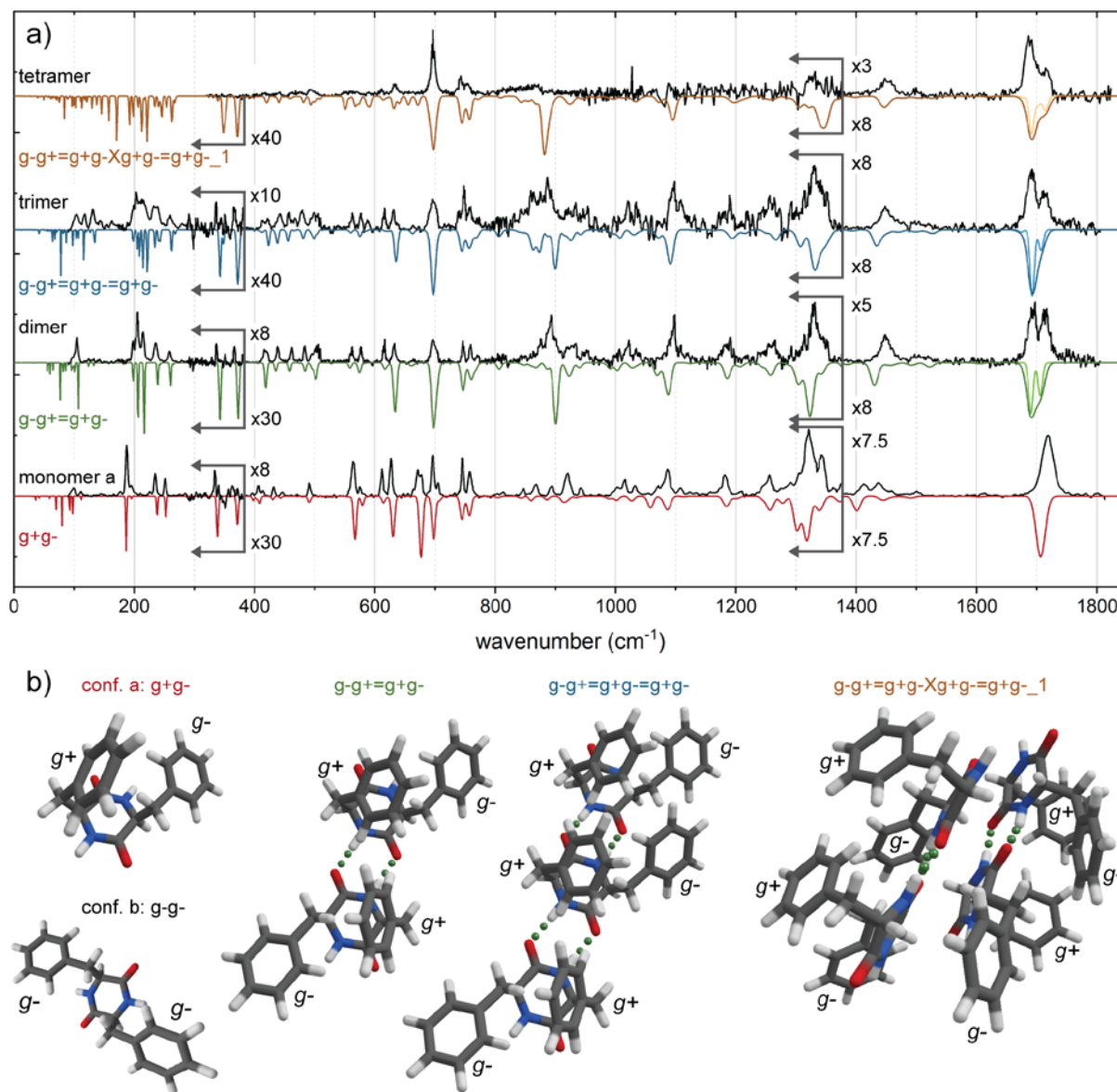


Figure SI.11: a) Overview of the experimental spectra (black traces), assigned calculated spectra (colored traces). The traces belong to $(\text{cyclo-FF})_n$ clusters, with $n=1-4$, from bottom to top. The calculated spectra are all scaled by 0.976 and are convoluted with 1% width of the wavenumber to match the characteristics of the infrared laser. For clarity, parts of the spectra are multiplied, as indicated in the figure. b) Assigned 3D structures.

12. XYZ files of assigned structures

Here, all xyz files of the optimized geometries of the assigned structures are presented, together with the input lines that were used in Gaussian 16.

Monomer

Conformer 1, g+g-

#p Opt=Tight B3LYP/6-311+G** EmpiricalDispersion=GD3 Int=(Grid=SuperFine,Acc2E=13) freq=noraman

N	-2.18903	-1.91789	0.41878
H	-3.02731	-2.14143	0.9403
C	-1.05446	-1.92751	1.16565
O	-1.04364	-2.21904	2.3507
C	0.24914	-1.58581	0.45211
H	0.90891	-2.43674	0.64748
C	0.88782	-0.32605	1.09123
C	4.64048	-0.50463	0.44597
C	3.38316	-0.72171	1.00503
C	2.25673	-0.04563	0.52081
C	2.41984	0.85264	-0.53967
C	3.67706	1.07055	-1.10337
C	4.79076	0.3919	-0.61254
H	5.50333	-1.03183	0.83763
H	3.27284	-1.41764	1.8311
H	1.5551	1.38666	-0.91767
H	3.78543	1.77118	-1.92392
H	5.76896	0.56185	-1.04782
H	0.22395	0.52358	0.92774
H	0.94309	-0.50647	2.16668
N	0.10039	-1.45442	-0.99443
H	0.9487	-1.29364	-1.52469
C	-2.35881	-1.3844	-0.92711
H	-2.9446	-2.10228	-1.50894
C	-1.04183	-1.23923	-1.68774
O	-1.06221	-0.94549	-2.87379
C	-3.12517	-0.03399	-0.93653
H	-3.31668	0.21584	-1.98182
H	-4.09429	-0.19563	-0.45413
C	-2.37946	1.0865	-0.2523
C	-2.50001	1.29636	1.12563
H	-3.15828	0.66189	1.70933
C	-1.51846	1.91432	-0.98403
H	-1.40745	1.75208	-2.0507
C	-1.78039	2.30777	1.76016
H	-1.88319	2.4518	2.82964
C	-0.80144	2.92873	-0.35271
H	-0.14312	3.56489	-0.93394
C	-0.92841	3.12753	1.02187
H	-0.36736	3.91418	1.51312

Conformer 2, g-g-

#p Opt=Tight B3LYP/6-311+G** EmpiricalDispersion=GD3 Int=(Grid=SuperFine,Acc2E=13) freq=noraman

N	1.19165	0.65851	-1.32951
H	2.0764	1.14895	-1.37877
C	0.10428	1.46325	-1.21142
O	0.16081	2.68154	-1.25263
C	-1.23959	0.76578	-1.01584
H	-1.92242	1.24429	-1.72173
C	-1.75996	1.04099	0.42117
C	-4.62665	-1.3275	1.27209
C	-3.34304	-0.79899	1.13759
C	-3.14943	0.4899	0.62848
C	-4.27154	1.23903	0.25525
C	-5.55512	0.71473	0.38994

C	-5.73611	-0.57183	0.89788
H	-4.75808	-2.32748	1.6698
H	-2.48354	-1.39291	1.4312
H	-4.13692	2.24209	-0.1376
H	-6.41383	1.31088	0.10205
H	-6.73467	-0.98009	1.00412
H	-1.06367	0.5945	1.1377
H	-1.74198	2.12269	0.57111
N	-1.19167	-0.65836	-1.32964
H	-2.07642	-1.1488	-1.37894
C	1.23956	-0.76566	-1.01584
H	1.92237	-1.24412	-1.72178
C	-0.10432	-1.46312	-1.21146
O	-0.16085	-2.6814	-1.25267
C	1.75995	-1.041	0.42113
H	1.06369	-0.59456	1.13772
H	1.74196	-2.12271	0.57099
C	3.14944	-0.48995	0.62846
C	3.34309	0.79886	1.13774
H	2.48361	1.39275	1.43148
C	4.27153	-1.23905	0.25507
H	4.13687	-2.24205	-0.13792
C	4.62671	1.32733	1.27226
H	4.75818	2.32726	1.6701
C	5.55512	-0.71478	0.38977
H	6.4138	-1.3109	0.10176
C	5.73615	0.5717	0.89789
H	6.73471	0.97993	1.00414

Dimer

Conformer a, g-g+=g+g-

#p Opt=Tight B3LYP/6-311+G** EmpiricalDispersion=GD3 Int=(Grid=SuperFine,Acc2E=13) freq=norman

N	-1.88795	-0.22094	-1.5315
H	-1.03378	-0.79866	-1.53579
C	-1.68469	1.10004	-1.52577
O	-0.56463	1.62335	-1.53332
C	-2.8925	2.02378	-1.46155
H	-2.7252	2.77377	-2.23966
C	-2.90484	2.76175	-0.09436
C	-2.03669	0.41509	2.77883
C	-1.91014	1.27672	1.69184
C	-3.04485	1.83785	1.09164
C	-4.3051	1.49676	1.59384
C	-4.43391	0.62625	2.67521
C	-3.29778	0.08636	3.27522
H	-1.14985	-0.00558	3.2393
H	-0.92996	1.51633	1.29751
H	-5.19499	1.9141	1.13468
H	-5.41962	0.37061	3.0468
H	-3.39419	-0.58837	4.11818
H	-1.97246	3.3265	-0.03275
H	-3.72938	3.48147	-0.11112
N	-4.14469	1.33733	-1.74285
H	-4.9774	1.90175	-1.85349
C	-3.17295	-0.9134	-1.50174
H	-3.20358	-1.59144	-2.36038
C	-4.38027	0.00102	-1.68977
O	-5.49794	-0.47586	-1.80828
C	-3.36092	-1.75054	-0.2152
H	-3.3316	-1.07942	0.64442
H	-4.36666	-2.176	-0.26574
C	-2.33929	-2.85379	-0.05202
C	-2.23454	-3.88121	-0.99709
H	-2.89034	-3.88538	-1.86216
C	-1.49093	-2.88345	1.05684
H	-1.56213	-2.09384	1.79571

C	-1.30539	-4.90524	-0.83988
H	-1.23883	-5.69099	-1.58428
C	-0.56621	-3.91359	1.22569
H	0.08088	-3.91823	2.09608
C	-0.46754	-4.92642	0.27543
H	0.25111	-5.72849	0.40302
N	-8.06943	0.63004	-1.76397
H	-7.23672	0.06563	-1.87461
C	-7.83385	1.96636	-1.71088
O	-6.71618	2.44324	-1.82938
C	-9.04117	2.88077	-1.52284
H	-9.01054	3.55881	-2.38148
C	-8.8532	3.71791	-0.2363
C	-10.90874	6.87261	-0.86098
C	-9.97958	5.84858	-1.01819
C	-9.87483	4.82116	-0.07313
C	-10.72319	4.85082	1.03574
C	-11.64791	5.88096	1.20458
C	-11.74659	6.89379	0.25433
H	-10.97529	7.65836	-1.60538
H	-9.32378	5.85275	-1.88326
H	-10.65199	4.06121	1.7746
H	-12.295	5.8856	2.07498
H	-12.46524	7.69586	0.38192
H	-8.88252	3.04679	0.62332
H	-7.84746	4.14338	-0.28685
N	-10.32617	2.18831	-1.55261
H	-11.18034	2.76603	-1.5569
C	-9.32162	-0.0564	-1.48266
H	-9.48892	-0.80639	-2.26078
C	-10.52943	0.86734	-1.54687
O	-11.64949	0.34403	-1.55442
C	-9.30927	-0.79438	-0.11548
H	-10.24165	-1.35914	-0.05386
H	-8.48473	-1.51409	-0.13225
C	-9.16926	0.12951	1.07052
C	-10.30397	0.69064	1.67072
H	-11.28415	0.45104	1.2764
C	-7.90901	0.4706	1.57272
H	-7.01912	0.05326	1.11357
C	-10.17741	1.55227	2.75771
H	-11.06426	1.97294	3.21818
C	-7.7802	1.34111	2.6541
H	-6.79449	1.59674	3.02569
C	-8.91633	1.881	3.25412
H	-8.81992	2.55572	4.09707

Trimer

Conformer a, g-g+=g+g-=g+g-

#p Opt=Tight B3LYP/6-311+G* EmpiricalDispersion=GD3 Int=(Grid=SuperFine,Acc2E=13) freq=noraman

N	7.5115	0.41296	-1.89432
H	8.50295	0.20772	-1.92817
C	7.20861	1.73304	-1.94857
O	8.05047	2.60516	-2.10182
C	5.73656	2.11251	-1.82354
H	5.51232	2.70371	-2.71623
C	5.51915	3.02914	-0.58844
C	7.49735	1.76999	2.41632
C	7.16005	2.43904	1.24113
C	5.86572	2.34932	0.7139
C	4.91831	1.5716	1.38966
C	5.25755	0.89147	2.55867
C	6.5484	0.99006	3.07628
H	8.50204	1.85485	2.81558
H	7.90459	3.02925	0.71791
H	3.91247	1.49982	0.98993

H	4.51972	0.27882	3.06324
H	6.81275	0.46177	3.98514
H	6.13515	3.918	-0.73586
H	4.47104	3.34029	-0.59037
N	4.83259	0.96956	-1.80055
H	3.82546	1.1887	-1.78099
C	6.63109	-0.67684	-1.48924
H	6.75088	-1.49654	-2.20465
C	5.1587	-0.30326	-1.55102
O	4.31638	-1.1965	-1.38103
C	6.97785	-1.21737	-0.0769
H	6.82358	-0.41861	0.64936
H	6.26627	-2.01513	0.14514
C	8.39611	-1.72825	-0.00851
C	8.7115	-3.01863	-0.45081
H	7.91753	-3.67119	-0.80123
C	9.43187	-0.90412	0.44539
H	9.19752	0.09489	0.79601
C	10.02748	-3.47535	-0.43825
H	10.25335	-4.47991	-0.77841
C	10.75097	-1.35752	0.45717
H	11.54133	-0.70602	0.81321
C	11.05244	-2.64408	0.01467
H	12.07683	-2.99868	0.02525
N	1.54455	-0.61066	-1.34956
H	2.54768	-0.83867	-1.41753
C	1.23038	0.68953	-1.38919
O	2.07462	1.58026	-1.55982
C	-0.22581	1.08864	-1.21338
H	-0.46768	1.71795	-2.07507
C	-0.364	1.94882	0.06888
C	-3.43039	4.17399	-0.35182
C	-2.1569	3.63446	-0.51472
C	-1.74338	2.53484	0.24515
C	-2.63833	1.98207	1.16365
C	-3.91173	2.52065	1.33378
C	-4.31104	3.62065	0.57788
H	-3.73387	5.02916	-0.94566
H	-1.47287	4.076	-1.23331
H	-2.32441	1.12566	1.74836
H	-4.59644	2.07277	2.04479
H	-5.30261	4.04009	0.70797
H	-0.1057	1.32917	0.92853
H	0.38204	2.7435	-0.00314
N	-1.14441	-0.04435	-1.21801
H	-2.14652	0.16434	-1.34579
C	0.65083	-1.71156	-1.02335
H	0.77768	-2.48752	-1.78438
C	-0.82116	-1.33414	-1.0875
O	-1.66197	-2.24354	-1.02602
C	1.00353	-2.35229	0.34757
H	0.38105	-3.24247	0.45596
H	2.04639	-2.67691	0.29498
C	0.80144	-1.41583	1.51303
C	-0.39994	-1.42051	2.23124
H	-1.17386	-2.13289	1.96857
C	1.79247	-0.49416	1.87035
H	2.73008	-0.48908	1.32563
C	-0.6071	-0.52566	3.2792
H	-1.53755	-0.55512	3.83489
C	1.58164	0.41215	2.9085
H	2.35011	1.13287	3.16256
C	0.38028	0.39917	3.61608
H	0.21623	1.10285	4.42404
N	-4.38719	-1.82519	-1.73961
H	-3.38295	-2.01202	-1.62884
C	-4.72161	-0.52694	-1.75062
O	-3.8881	0.38381	-1.79647
C	-6.19572	-0.15907	-1.69812
H	-6.36603	0.50588	-2.55019
C	-6.46509	0.64047	-0.39748

C	-9.51604	2.84853	-0.96705
C	-8.20673	2.37288	-0.97884
C	-7.87421	1.17224	-0.33953
C	-8.8857	0.45819	0.31261
C	-10.19812	0.93069	0.32467
C	-10.51699	2.12668	-0.31587
H	-9.75569	3.78296	-1.4625
H	-7.42961	2.93914	-1.48323
H	-8.63669	-0.46845	0.81842
H	-10.96978	0.36537	0.83548
H	-11.53614	2.4962	-0.30556
H	-6.2647	-0.00819	0.45681
H	-5.74212	1.45563	-0.37336
N	-7.07786	-1.31287	-1.8343
H	-8.07289	-1.12367	-1.85701
C	-5.27693	-2.95093	-1.48392
H	-5.09266	-3.71198	-2.24846
C	-6.75921	-2.61083	-1.6092
O	-7.59501	-3.49857	-1.52424
C	-4.98422	-3.59718	-0.10369
H	-5.60577	-4.49123	-0.02899
H	-3.93721	-3.9116	-0.10347
C	-5.24977	-2.66503	1.05366
C	-4.26386	-1.77485	1.49539
H	-3.29672	-1.76912	1.00449
C	-6.50388	-2.64408	1.67665
H	-7.27817	-3.31975	1.32937
C	-4.52323	-0.89444	2.54426
H	-3.75103	-0.21204	2.87677
C	-6.76436	-1.76062	2.72262
H	-7.73971	-1.75811	3.19662
C	-5.773	-0.88341	3.16135
H	-5.97391	-0.19674	3.97599

Tetramer

g+g-=g+g-Xg+g-=g+g-

#p B3LYP/6-31+G* Guess=Read EmpiricalDispersion=GD3 Int=(Grid=SuperFine,Acc2E=13) freq=noraman

Geom=AllCheck

N	-7.23826	-4.54542	1.42612
H	-8.12137	-4.76386	1.91492
C	-7.20657	-4.80813	0.11231
O	-8.19678	-5.23134	-0.51373
C	-5.90605	-4.58256	-0.64394
H	-6.15482	-3.92799	-1.48777
C	-5.40665	-5.93838	-1.21175
C	-3.23468	-5.22433	-4.2717
C	-4.34687	-5.35381	-3.43717
C	-4.20384	-5.79902	-2.11508
C	-2.92029	-6.10138	-1.64477
C	-1.80503	-5.97861	-2.47594
C	-1.9591	-5.54155	-3.79378
H	-3.36374	-4.88124	-5.29531
H	-5.33868	-5.11477	-3.81739
H	-2.80407	-6.43709	-0.61844
H	-0.81544	-6.20746	-2.08961
H	-1.09123	-5.44405	-4.44154
H	-5.1747	-6.59824	-0.37164
H	-6.24692	-6.38005	-1.75789
N	-4.88347	-3.91049	0.15176
H	-4.07779	-3.51456	-0.35952
C	-6.10853	-4.18307	2.2698
H	-6.40139	-3.3139	2.87083
C	-4.8893	-3.73258	1.47853
O	-3.94561	-3.20725	2.10002
C	-5.74413	-5.32447	3.26246
H	-4.98067	-4.92973	3.94027

H	-6.64165	-5.53519	3.85584
C	-5.2558	-6.57859	2.57699
C	-3.88404	-6.79847	2.38052
H	-3.1684	-6.07545	2.76327
C	-6.16566	-7.52419	2.0803
H	-7.2298	-7.36595	2.23626
C	-3.4319	-7.93375	1.70322
H	-2.36477	-8.09416	1.57314
C	-5.71718	-8.65347	1.38951
H	-6.43366	-9.36701	0.99206
C	-4.34788	-8.86132	1.19863
H	-3.99842	-9.73904	0.66146
N	-1.88314	-1.76717	0.75217
H	-2.70224	-2.16024	1.23641
C	-1.81512	-2.04306	-0.56038
O	-2.74263	-2.5813	-1.18641
C	-0.54216	-1.68431	-1.3126
H	-0.85723	-1.07762	-2.16992
C	0.10701	-2.98734	-1.8519
C	2.24283	-2.1012	-4.88915
C	1.14159	-2.4036	-4.08472
C	1.30634	-2.70799	-2.72447
C	2.6025	-2.70233	-2.18762
C	3.70732	-2.39796	-2.98901
C	3.53054	-2.09598	-4.34217
H	2.09713	-1.87285	-5.94215
H	0.14121	-2.41033	-4.51413
H	2.74117	-2.94533	-1.13688
H	4.70464	-2.39869	-2.55605
H	4.38855	-1.8614	-4.9669
H	0.38764	-3.61371	-1.00023
H	-0.66688	-3.51675	-2.41279
N	0.38635	-0.8933	-0.51123
H	1.2345	-0.58017	-0.97462
C	-0.78916	-1.32619	1.60959
H	-1.14654	-0.47975	2.20862
C	0.42029	-0.79948	0.84194
O	1.36148	-0.29792	1.45373
C	-0.36186	-2.44684	2.59734
H	0.37989	-2.01248	3.27465
H	-1.24399	-2.71516	3.19004
C	0.19615	-3.66862	1.90455
C	-0.65596	-4.68714	1.45109
H	-1.72692	-4.59511	1.61348
C	1.57432	-3.78534	1.66421
H	2.2395	-2.99239	1.99777
C	-0.13917	-5.80252	0.78682
H	-0.81004	-6.58467	0.44467
C	2.09078	-4.89748	0.99411
H	3.16081	-4.97311	0.81679
C	1.23475	-5.91241	0.55555
H	1.63475	-6.77962	0.03623
N	-11.63334	-3.84794	0.93006
H	-12.42771	-4.4853	0.75893
C	-11.45795	-3.44501	2.19615
O	-12.16308	-3.85578	3.13722
C	-10.35363	-2.44221	2.49452
H	-9.74157	-2.89079	3.28607
C	-10.9875	-1.13871	3.05053
C	-8.37908	0.6322	5.20706
C	-9.3257	-0.29509	4.76636
C	-9.96406	-0.13532	3.52798
C	-9.62489	0.96859	2.73651
C	-8.68279	1.90177	3.17395
C	-8.0581	1.73762	4.41261
H	-7.8962	0.49521	6.17154
H	-9.57886	-1.14856	5.39317
H	-10.1098	1.09067	1.77239
H	-8.42452	2.74633	2.54076
H	-7.32317	2.46277	4.75369
H	-11.61197	-0.69942	2.26819

H	-11.64667	-1.43489	3.87344
N	-9.48194	-2.18502	1.35238
H	-8.58436	-1.71153	1.54591
C	-10.95958	-3.32807	-0.25111
H	-10.60398	-4.18203	-0.83996
C	-9.71339	-2.51872	0.07681
O	-8.9523	-2.20516	-0.85872
C	-11.93226	-2.51996	-1.15767
H	-11.3889	-2.27722	-2.07635
H	-12.75751	-3.19067	-1.42438
C	-12.45956	-1.26691	-0.49966
C	-11.82181	-0.0328	-0.69693
H	-10.96463	0.02349	-1.36287
C	-13.5673	-1.32087	0.35982
H	-14.07272	-2.27137	0.51102
C	-12.27782	1.11884	-0.05055
H	-11.77964	2.06866	-0.22687
C	-14.01688	-0.17345	1.0193
H	-14.86296	-0.23368	1.69823
C	-13.37256	1.05053	0.81598
H	-13.72142	1.94309	1.32854
N	-6.30817	-1.24443	-0.3793
H	-7.20338	-1.72559	-0.54359
C	-6.12346	-0.80544	0.87637
O	-6.88454	-1.09783	1.81294
C	-4.93068	0.0947	1.16265
H	-4.38908	-0.37431	1.99275
C	-5.44835	1.47816	1.64033
C	-2.73076	3.11309	3.76484
C	-3.79904	2.3039	3.37079
C	-4.32522	2.38907	2.07235
C	-3.75521	3.30547	1.17593
C	-2.68425	4.11575	1.56579
C	-2.16857	4.02148	2.86142
H	-2.33918	3.03741	4.77633
H	-4.23666	1.60056	4.0772
H	-4.16157	3.3849	0.17049
H	-2.25518	4.82061	0.85786
H	-1.33761	4.65222	3.16665
H	-6.02284	1.9332	0.82832
H	-6.13587	1.2892	2.46821
N	-4.01883	0.20576	0.02853
H	-3.17629	0.75439	0.17432
C	-5.59607	-0.80223	-1.57254
H	-5.29335	-1.69237	-2.13736
C	-4.30186	-0.05053	-1.27349
O	-3.55815	0.27708	-2.19613
C	-6.51637	0.04314	-2.49584
H	-5.95367	0.2451	-3.41246
H	-7.37828	-0.58064	-2.75936
C	-6.97778	1.33213	-1.85575
C	-8.12307	1.36002	-1.04541
H	-8.68612	0.44316	-0.89003
C	-6.24315	2.51619	-2.02624
H	-5.34513	2.49911	-2.63922
C	-8.5314	2.5478	-0.43318
H	-9.42168	2.55534	0.18829
C	-6.6475	3.70274	-1.40879
H	-6.06791	4.61143	-1.5518
C	-7.79625	3.7229	-0.61183
H	-8.11394	4.64549	-0.13258