

SUPPORTING INFORMATION

ADDITIVE MODEL FOR THE SECOND HARMONIC GENERATION HYPERPOLARIZABILITY APPLIED TO A COLLAGEN-MIMICKING PEPTIDE (PRO-PRO-GLY)₁₀

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1. COMPARISON OF COMPUTED AND EXPERIMENTAL GEOMETRIES

In the following, we compare the C_s geometry used for the hyperpolarizability calculation and the experimental geometries gathered by Serrano-Andr s in the Supporting Information of reference [SAF96].

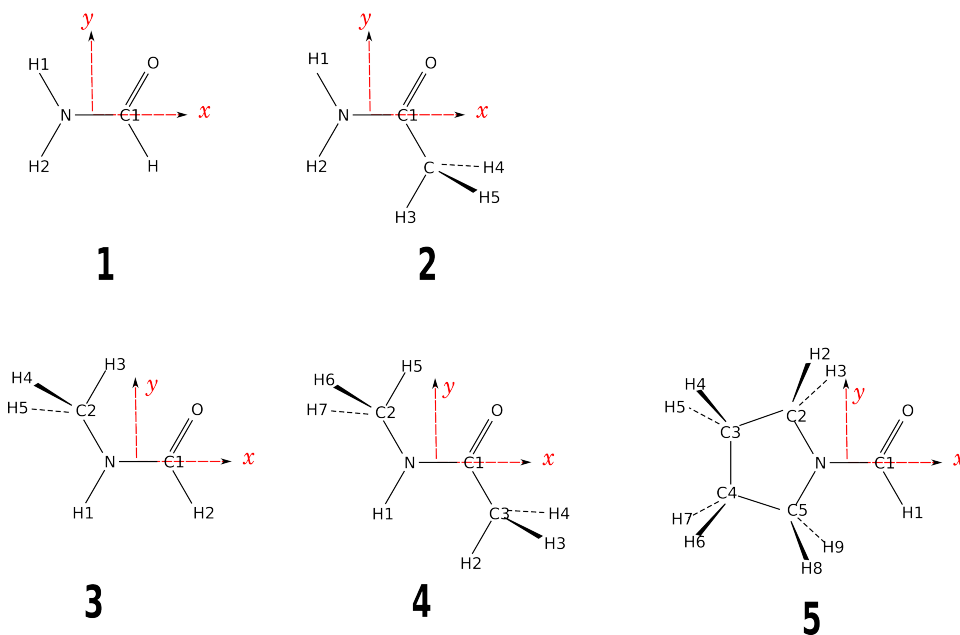


FIGURE S1. Structure and labeling of the studied amides (C_s symmetry). **1** formamide ; **2** acetamide ; **3** N-methylformamide; **4** N-methylacetamide; **5** N-azolidineformamide.

Among the different methyl orientation compatible with the C_s symmetry group, the lowest energy conformation was selected. The orientation was not always the same as the one described in [SAF96]. For molecules **1,2,3,4**, all the frequencies obtained by analytical derivative were positive in C_s symmetry group. For molecules **5**, two frequencies were negative; the geometry was then slightly deformed and re-optimized in C_1 symmetry group in which all the frequencies obtained by analytical derivative were positive.

TABLE S1. Bond lengths and angles of formamide and acetamide. Data gathered from SI of reference [SAF96] and reference therein.

Bonds ^a	Exp ^{b,e}	Theo ^c	Angles ^a	Exp ^{b,e}	Theo ^c	Dihedral angles ^a	Exp ^{b,e}	Theo ^c
Formamide (1)								
C ₁ O	1.212	1.220	NC ₁ O	125.0	124.7	OC ₁ NH ₁	0.0	0.0
C ₁ N	1.368	1.364	C ₁ NH ₁	118.7	119.2	OC ₁ NH ₁	180.0	180.0
H ₁ N	1.027 ^d	1.014	C ₁ NH ₂	119.7	121.5	H ₃ C ₁ NH ₁	180.0	180.0
H ₃ C ₁	1.125	1.113	NC ₁ H ₃	112.7	112.3			
Acetamide (2)								
C ₁ O	1.220	1.225	NC ₁ O	122.0	122.1	NC ₁ C ₂ O	0	0
C ₁ N	1.380	1.371	NC ₁ C ₂	115.1	115.7			
C ₁ C ₂	1.519	1.522	C ₁ C ₂ O	123.0	122.3			
H ₁ N	1.022 ^d	1.013	C ₁ NH ₁	118.5	118.5			
H ₂ N	1.022 ^d	1.010	C ₁ NH ₂	120.0	122.3			
H ₃ C ₂	1.124 ^d	1.097	C ₁ C ₂ H ₃	109.8 ^d	114.1			
H ₄ C ₂	1.124 ^d	1.097	C ₁ C ₂ H ₄	109.8 ^d	108.5			
H ₅ C ₂	1.124 ^d	1.097	C ₁ C ₂ H ₅	109.8 ^d	108.5			

^a Bonds in Å, angles in degrees. See Figure S1 for atom labeling.

^b Gas-phase electron diffraction, $\pm 0.01\text{Å}$, $\pm 1^\circ$ [KK74a, KK73].

^c Our work : BP86/QZ4P calculation, C_s symmetry.

^d Average values

TABLE S2. Bond lengths and angles of N-methylformamide and N-methylacetamide.

Bonds ^a	Exp ^b	Theo ^c	Angles ^a	Exp ^b	Theo ^c	Dihedral angles ^a	Exp ^b	Theo ^c
N-methylformamide (3)								
C ₁ O	1.219	1.223	NC ₁ O	124.6	126.3	OC ₁ NC ₂	0	
C ₁ N	1.366	1.364	C ₁ NC ₂	121.4	123.1	C ₁ NC ₂ H ₄	60	
C ₂ N	1.459	1.455	H ₁ NC ₁	118.7	117.6	C ₁ NC ₂ H ₅	-60	
H ₁ N	1.027	1.014	NC ₁ H ₂	112.7	111.8			
H ₂ C ₁	1.125	1.113	NC ₂ H ₃	108.8 ^e	107.4			
H ₃ C ₂	1.114 ^d	1.094	NC ₂ H ₄	110.6 ^e	111.2			
H ₄ C ₃	1.114 ^d	1.098	NC ₂ H ₅	110.6 ^e	111.2			
H ₅ C ₂	1.114 ^d	1.098						
N-methylacetamide (4)								
C ₁ O	1.220	1.225	NC ₁ O	122.0	122.1	NC ₁ C ₂ O	0	0
C ₁ N	1.380	1.371	NC ₁ C ₂	115.1	115.7			
C ₁ C ₂	1.519	1.522	C ₁ C ₂ O	123.0	122.3			
H ₁ N	1.022 ^d	1.013	C ₁ NH ₁	118.5	118.5			
H ₂ N	1.022 ^d	1.010	C ₁ NH ₂	120.0	122.3			
H ₃ C ₂	1.124 ^d	1.097	C ₁ C ₂ H ₃	109.8 ^d	114.1			
H ₄ C ₂	1.124 ^d	1.097	C ₁ C ₂ H ₄	109.8 ^d	108.5			
H ₅ C ₂	1.124 ^d	1.097	C ₁ C ₂ H ₅	109.8 ^d	108.5			

^a Bonds in Å, angles in degrees. See Figure S1 for atom labeling.^b Gas-phase electron diffraction $\pm 0.01\text{\AA}$, $\pm 1^\circ$ [KFK73, KK74b].^c Our work: BP86/QZ4P calculation, C_s symmetry.^d Average values

TABLE S3. Bond lengths and angles of N-azolidineformamide.

Bonds ^a	Theo ^b	Theo ^c	Angles ^a	Theo ^b	Theo ^c	Dihedral angles ^a	Theo ^b	Theo ^c
N-azolidineformamide (5)								
C ₁ O	1.228	1.227	NC ₁ O	125.0	124.7	C ₂ NC ₁ O	-2.1	0
C ₁ N	1.359	1.358	NC ₂ H ₁	112.3	112.6	C ₂ NC ₁ H ₁	177.7	180
C ₁ H ₁	1.113	1.113	C ₁ NC ₂	122.5	121.3	C ₁ NC ₂ C ₃	-158.8	0
C ₂ N	1.464	1.463	NC ₁ C ₃	104.9	105.5	C ₂ C ₃ C ₄ C ₅	-6.6	0
C ₅ N	1.463	1.466	C ₂ C ₃ C ₄	106.6	107.2			
C ₂ C ₃	1.546	1.544	C ₃ C ₄ C ₅	106.3	107.4			
C ₃ C ₄	1.553	1.548	C ₄ C ₅ N	104.3	105.2			
C ₄ C ₅	1.543	1.546	C ₄ NC ₂	112.4	114.7			
C ₂ H ₂	1.096	1.099	NC ₂ H ₂	109.0	109.9			
C ₃ H ₄	1.096	1.096	C ₂ C ₃ H ₄	110.7	110.6			
C ₄ H ₆	1.096	1.096	C ₃ C ₄ H ₆	111.2	111.1			
C ₅ H ₈	1.098	1.100	C ₄ C ₅ H ₈	113.0	111.6			

^a Bonds in Å, angles in degrees. See Figure S1 for atom labeling.

^b Our work : BP86/QZ4P calculation, C₁ symmetry.

^c Our work : BP86/QZ4P calculation, C_s symmetry.

2. XYZ FILES FOR THE CORRESPONDING GEOMETRIES

Geometry 1 , Formamide optimized with BP86/QZ4P (ADF2007) in Cs

6

coordinates in Angstrom

C	0.7341850000	0.0000000000	0.0000000000
N	-0.6295610000	-0.0000000000	0.0000000000
O	1.4288090000	1.0024230000	0.0000000000
H	1.1563430000	-1.0299650000	0.0000000000
H	-1.1235610000	0.8857190000	0.0000000000
H	-1.1586260000	-0.8619640000	0.0000000000

Geometry 2 , Acetamide optimized with BP86/QZ4P (ADF2007) in Cs

9

coordinates in Angstrom

C	0.7380540000	0.0000000000	0.0000000000
N	-0.6328790000	0.0000000000	0.0000000000
O	1.3890280000	1.0382360000	0.0000000000
H	0.6888410000	-2.2087370000	0.0000000000
C	1.3968740000	-1.3714760000	0.0000000000
H	-1.1161070000	0.8899470000	0.0000000000
H	-1.1728730000	-0.8536230000	0.0000000000
H	2.0440600000	-1.4460710000	0.8823790000
H	2.0440600000	-1.4460710000	-0.8823790000

Geometry 3 , N-methyl Formamide optimized with BP86/QZ4P (ADF2007)
in Cs.

9

coordinates in Angstrom

C	0.7341160000	-0.0000000000	0.0000000000
N	-0.6295020000	0.0000000000	0.0000000000
O	1.4416190000	0.9976020000	0.0000000000
C	-1.4248780000	1.2187690000	0.0000000000
H	-1.0993110000	-0.8982750000	0.0000000000
H	-0.7297330000	2.0639460000	0.0000000000
H	1.1475800000	-1.0331010000	0.0000000000
H	-2.0613070000	1.2772020000	0.8932800000
H	-2.0613070000	1.2772020000	-0.8932800000

Geometry 4 , N-methylacetamide optimized with BP86/QZ4P (ADF2007)
in Cs

12

coordinates in Angstrom

C	0.7378900000	0.0000000000	0.0000000000
N	-0.6327390000	-0.0000000000	0.0000000000
O	1.4019530000	1.0344130000	0.0000000000
C	-1.4154290000	1.2260280000	0.0000000000
C	1.3885480000	-1.3737360000	0.0000000000
H	-1.1166000000	-0.8893280000	0.0000000000
H	0.6732100000	-2.2054170000	0.0000000000
H	-0.7067340000	2.0607970000	0.0000000000
H	2.0333400000	-1.4556410000	0.8834840000
H	-2.0503350000	1.2933250000	0.8937660000
H	-2.0503350000	1.2933250000	-0.8937660000
H	2.0333400000	-1.4556410000	-0.8834840000

Geometry 5 , N-azolidineformamide optimized with BP86/QZ4P (ADF2007)
in Cs

16

coordinates in Angstrom

C	0.7308750000	-0.0000000000	0.0000000000
N	-0.6267230000	0.0000000000	0.0000000000
O	1.4299360000	1.0088760000	0.0000000000
C	-1.4479760000	-1.2148710000	0.0000000000
C	-2.9110490000	-0.7160800000	0.0000000000
C	-2.8719420000	0.8318680000	0.0000000000
C	-1.3861150000	1.2507390000	0.0000000000
H	1.1578110000	-1.0275260000	0.0000000000
H	-3.3870850000	1.2381860000	0.8777190000
H	-3.4446400000	-1.0965610000	0.8779930000
H	-1.1148890000	1.8521550000	0.8793120000
H	-1.2305000000	-1.8313990000	0.8850860000
H	-1.2305000000	-1.8313990000	-0.8850860000
H	-1.1148890000	1.8521550000	-0.8793120000
H	-3.4446400000	-1.0965610000	-0.8779930000
H	-3.3870850000	1.2381860000	-0.8777190000

Remark : this geometry has two negative frequencies.

Geometry 5 bis , N-azolidineformamide optimized with BP86/QZ4P (ADF2007)
in C1

16

coordinates in Angstrom

C	0.7317420000	-0.0000000000	-0.0000000000
N	-0.6274660000	0.0000000000	0.0000000000
O	1.4362650000	1.0061360000	-0.0000000000
C	-1.4137710000	1.2339180000	-0.0447460000
C	-2.7943300000	-0.7518790000	-0.6148660000
C	-2.8023530000	0.8009010000	-0.5700130000
C	-1.4698840000	-1.1960050000	0.0414370000
H	-2.8626930000	-1.1195810000	-1.6454450000
H	-2.9851470000	1.2131990000	-1.5693490000
H	-0.9018090000	1.9592370000	-0.6869630000
H	-0.9796430000	-2.0192100000	-0.4942900000
H	-3.6512120000	-1.1706600000	-0.0742180000
H	1.1544620000	-1.0298700000	-0.0038070000
H	-3.5998410000	1.1773290000	0.0803320000
H	-1.4802780000	1.6863490000	0.9575780000
H	-1.6395190000	-1.5328410000	1.0788670000

3. DETERMINATION OF THE DECORRELATION TIME OF PPG₁₀

The structural decorrelation time was calculated using Lyman's method [LZ06]. The solvent and counter-ions' positions were not taken into account in the analysis. The curves were averaged over 400 different structural decompositions. The variances were calculated with subsamples of length $n = 2, 3, 4, 5$, and the trajectory was decomposed into 10 bins.

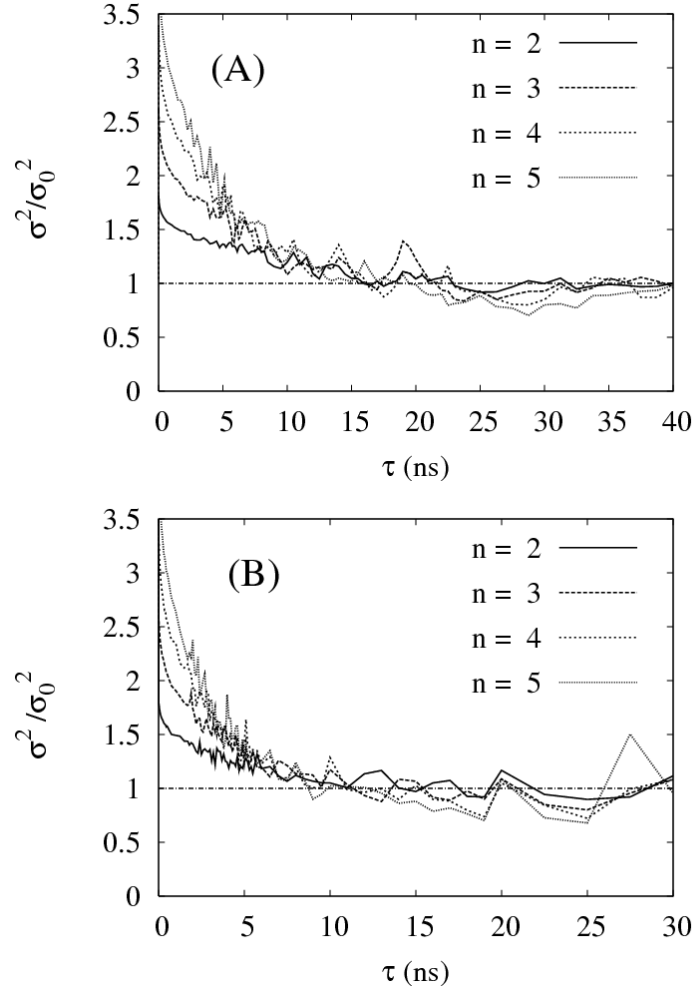


FIGURE S2. (A): Rescaled variance $(\sigma/\sigma_0)^2$ as a function of the time τ between two configurations of the trajectory subsamples of size n for the zwitterion simulations. (B) : Same for the cation simulations. Note the difference in the time ranges.

4. HYPERPOLARIZABILITY TENSOR OF NMA (SAOP/QZ4P)

Static and at 800 nm. Output of ADF calculation.

For the first column, the convention T=AB of Willetts et al. (J.Chem.Phys. vol. 97, p.7590 (1992)) is used

which is the convention commonly used by theoreticians for calculations on small molecules.

In the second column this number is divided by two (this corresponds better to certain experimental conventions).

The third and fourth column give the same information in electrostatic units (esu) instead of atomic units (a.u.).

The STATIC hyperpolarizability tensor beta

Non-zero components of beta:

beta(y z z) =	3.9490	1.9745	0.34117E-31	0.17058E-31
beta(x z z) =	14.667	7.3337	0.12671E-30	0.63357E-31
beta(z y z) =	3.9490	1.9745	0.34117E-31	0.17058E-31
beta(z x z) =	14.667	7.3337	0.12671E-30	0.63357E-31
beta(z z y) =	3.9490	1.9745	0.34117E-31	0.17058E-31
beta(y y y) =	88.245	44.123	0.76237E-30	0.38118E-30
beta(x y y) =	30.226	15.113	0.26113E-30	0.13057E-30
beta(y x y) =	30.226	15.113	0.26113E-30	0.13057E-30
beta(x x y) =	23.732	11.866	0.20503E-30	0.10251E-30
beta(z z x) =	14.667	7.3337	0.12671E-30	0.63357E-31
beta(y y x) =	30.226	15.113	0.26113E-30	0.13057E-30
beta(x y x) =	23.732	11.866	0.20503E-30	0.10251E-30
beta(y x x) =	23.732	11.866	0.20503E-30	0.10251E-30
beta(x x x) =	-27.066	-13.533	-0.23383E-30	-0.11691E-30

The SHG hyperpolarizability tensor β
 Non-zero components of β :

$\beta(y\ z\ z) =$	4.5689	2.2845	$0.39472E-31$	$0.19736E-31$
$\beta(x\ z\ z) =$	17.359	8.6795	$0.14997E-30$	$0.74984E-31$
$\beta(z\ y\ z) =$	3.4537	1.7268	$0.29837E-31$	$0.14919E-31$
$\beta(z\ x\ z) =$	18.418	9.2088	$0.15911E-30$	$0.79557E-31$
$\beta(z\ z\ y) =$	3.4537	1.7268	$0.29837E-31$	$0.14919E-31$
$\beta(y\ y\ y) =$	112.70	56.351	$0.97366E-30$	$0.48683E-30$
$\beta(x\ y\ y) =$	27.537	13.769	$0.23790E-30$	$0.11895E-30$
$\beta(y\ x\ y) =$	31.064	15.532	$0.26837E-30$	$0.13419E-30$
$\beta(x\ x\ y) =$	36.482	18.241	$0.31518E-30$	$0.15759E-30$
$\beta(z\ z\ x) =$	18.418	9.2088	$0.15911E-30$	$0.79557E-31$
$\beta(y\ y\ x) =$	31.064	15.532	$0.26837E-30$	$0.13419E-30$
$\beta(x\ y\ x) =$	36.482	18.241	$0.31518E-30$	$0.15759E-30$
$\beta(y\ x\ x) =$	31.073	15.537	$0.26845E-30$	$0.13423E-30$
$\beta(x\ x\ x) =$	-46.598	-23.299	$-0.40257E-30$	$-0.20128E-30$

5. INFLUENCE OF THE BASIS SET AND FUNCTIONAL

TABLE S4. Influence of the basis set choice on several observables for formamide with the geometry and orientation defined in Fig. S1. First hyperpolarizabilities are given in B convention, in atomic units, for an incident wavelength of 800 nm.

Observable	ATZ2P	pVQZ	QZ4P
ΔE , NV1 (eV)	7.62	7.70	7.69
f , NV1	0.289	0.299	0.293
μ_x , NV1 (a.u.)	1.18	1.20	1.19
μ_y , NV1 (a.u.)	0.380	0.40	0.38
β_{yyyy}	60.2	60.0	65.9
β_{xxx}	34.0	29.9	34.6
β_{xyy}	21.2	21.5	22.7
β_{xzz}	13.8	12.0	12.8
β_{yxx}	9.9	10.6	11.0
β_{yzz}	7.6	6.6	7.6
$ \beta $	-61.0	-58.3	-49.5
D	0.117	0.122	0.120

TABLE S5. Influence of the functional choice on first hyperpolarizabilities for formamide (QZ4P basis set) with the geometry and orientation defined in Fig. S1. First hyperpolarizabilities are given in B convention, in atomic units, for an incident wavelength of 800 nm.

Observable	BP86	SAOP	ratio
β_{yyyy}	108.5	65.9	1.7
β_{xxx}	76.1	34.6	2.2
β_{xyy}	43.2	22.7	1.9
β_{xzz}	20.4	12.8	1.6
β_{xxy}	18.3	11.0	1.7
β_{yzz}	11.1	7.6	1.5
$ \beta $	-115.8	-49.5	2.4
D	0.12	0.12	1.0

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