Structure of Pb^{2+}/deprotonated dGMP complexes in the gas phase: A combined MS-MS/IRMPD spectroscopy/ion mobility study.

Jean-Yves Salpin[1,2], Luke MacAleese*[3,4], Fabien Chirot[5,6], Philippe Dugourd[3,4],*

1) Université d'Evry Val d'Essonne – Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement – Boulevard François Mitterrand – 91025 Evry – France
2) CNRS- UMR 8587.

3) Université Lyon 1– Institut Lumière Matière, 5 rue de la Doua, 69622 Villeurbanne cedex – France

4) CNRS- UMR 5306.

5) Université Lyon 1 – Institut des Sciences Analytiques, 5 rue de la Doua, 69100 Villeurbanne – France

6) CNRS- UMR 5280

Supporting information

1S. Low-energy CID spectrum of the $[Pb(GMP)-H]^+$ complex recorded at 30 eV (laboratory frame).

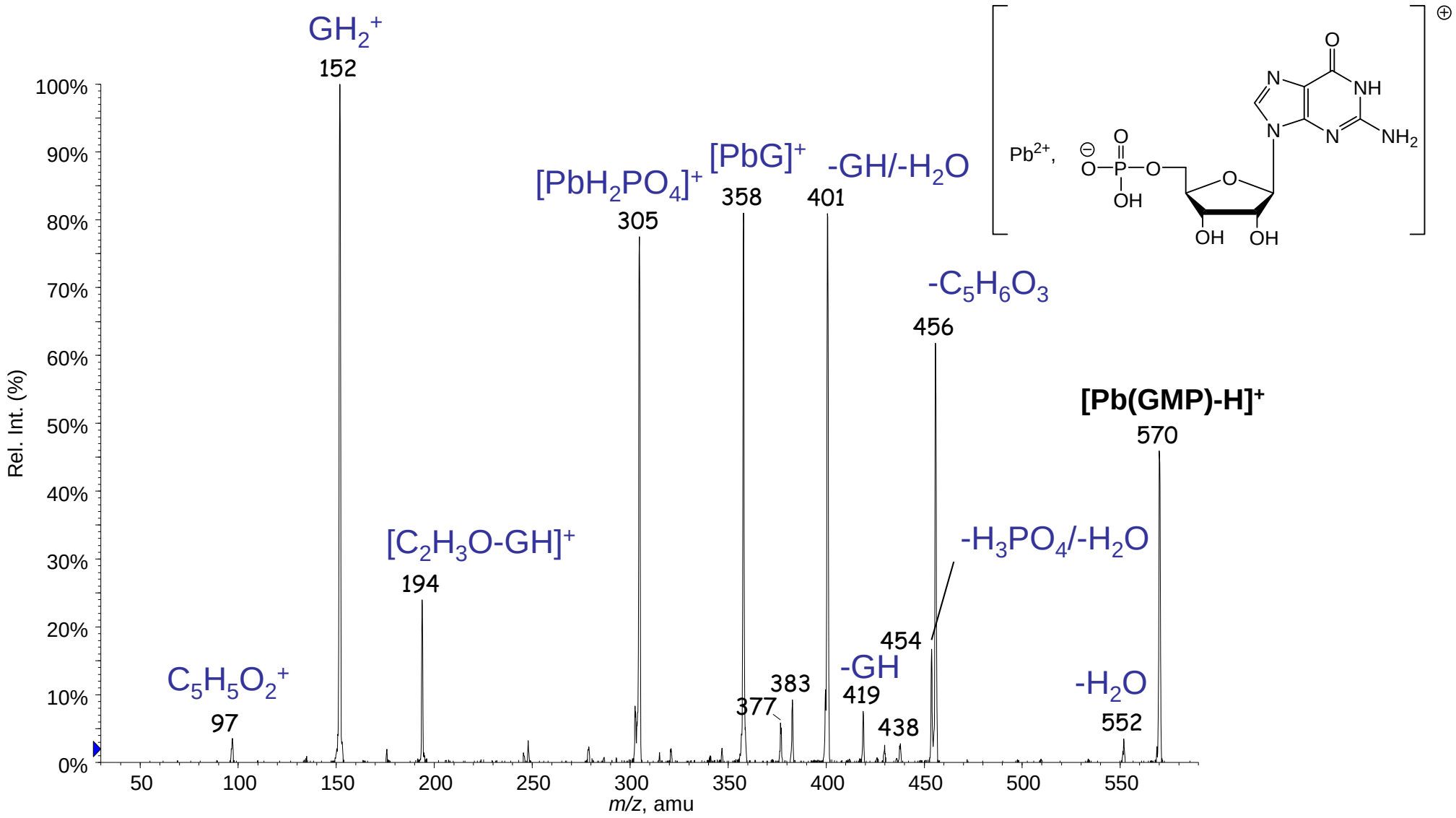
2S. Structure and geometrical details of the various structures optimized for the $[Pb(dGMP)-H^+$ complex

3S. Total energy and ZPE (Hartree) of the various structures considered

4S. DFT-computed IR absorption spectra for the $[Pb(dGMP)-H]^+$ structures. The experimental IRMPD spectrum is overlayed in grey.

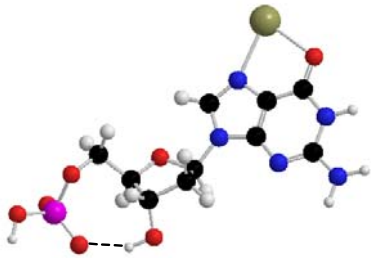
5S. Evolution of $[Pb(dGMP)-H]^+$ arrival time as a function of 1/E, the electric field applied across the mobility tube.

1S. Low-energy CID spectrum of the [Pb(GMP)-H]$^+$ complex recorded at 30 eV (laboratory frame).

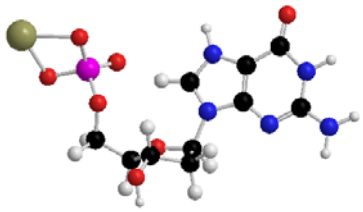


2S. Structure and geometrical details of the various structures optimized for the [Pb(dGMP)-H]$^{+}$ complex. Relative free energies determined at the B3LYP/6-31++G(2df,2p)//B3LYP/6-31G(d,p) level

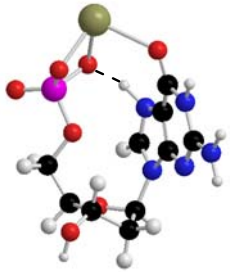
2.1 *Anti* forms



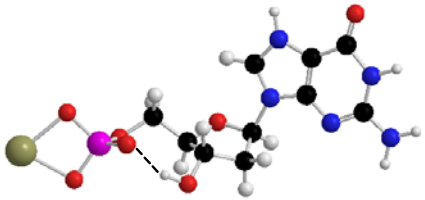
dGMPA1 +366.7



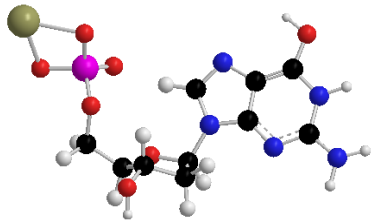
dGMPA2 +74.3



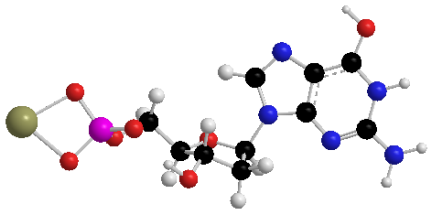
dGMPA3 +108.3



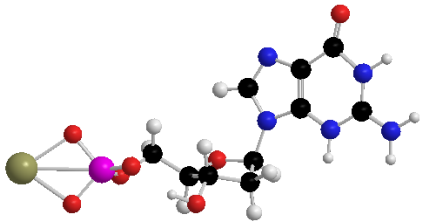
dGMPA4 +90.8



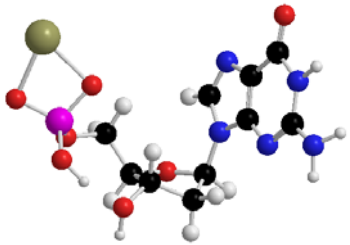
dGMPA5 +143.3



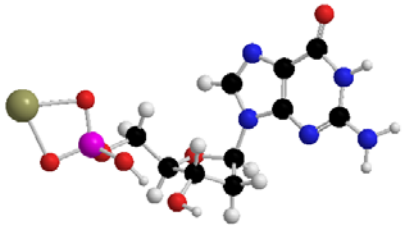
dGMPA6 +132.4



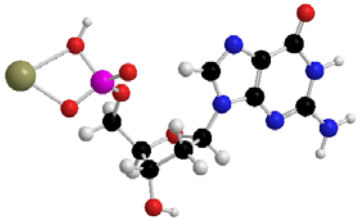
dGMPA7 +173.6



dGMPA8 +153.4

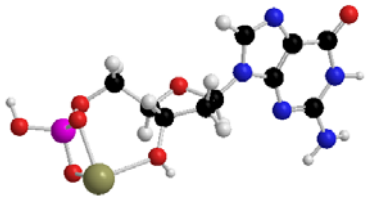


dGMPA9 +147.3

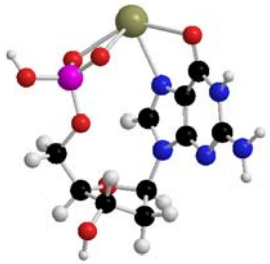


dGMPA10 +267.3*

dGMPA11 +145.9



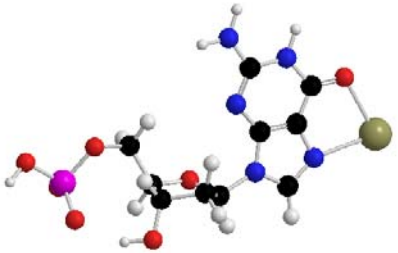
dGMPA12 +125.9



dGMPA13 +1.8

***B3LYP/6-31G(d,p)**

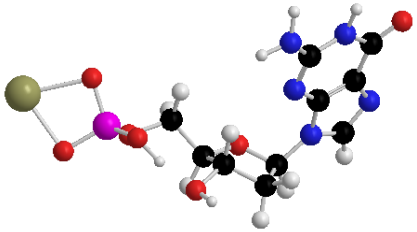
2.2 *Syn* forms



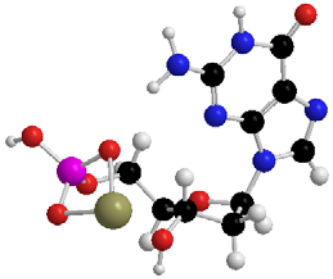
dGMPS1 +383.0*

*** B3LYP/6-31G(d,p)**

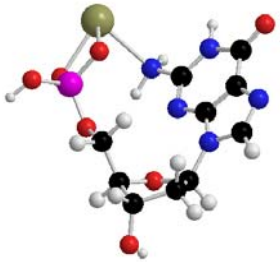
dGMPS2 +119.6



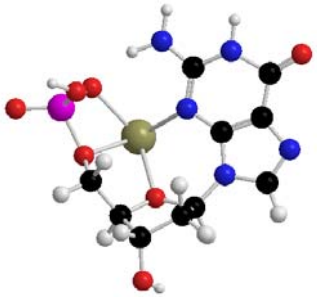
dGMPS3 +144.4



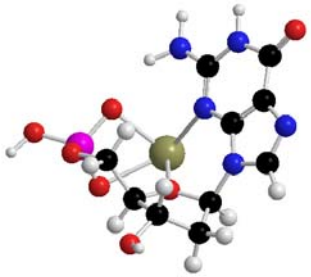
dGMPS4 +126.4



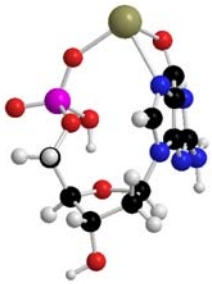
dGMPS5 +161.5



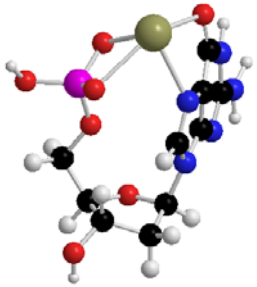
dGMPS6 +130.8



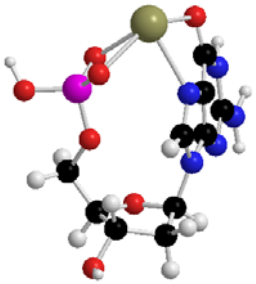
dGMPS7 +85.0



dGMPS8 +74.8



dGMPS9 +9.5



dGMPS10 0.0

2.3 Summary

Structures	Interaction sites									Sugar conformation[(a)]	Intramolecular H bonds
	Phopshate	O4'	OH 3'	OH 5'	C=O (6)	NH_2	N1	N3	N7		
***Anti forms*[(b)]**											
dGMPA1					O				O	C2'-endo/C1'-exo ($^2T_1$)	
dGMPA2	O (O^-/O^-)									C3'-endo/C2'-exo ($^3T_2$)	
dGMPA3	O (O^-/O^-)				O					C3'-endo/C2'-exo ($^3T_2$)	NH(7) → Phos (O^-)
dGMPA4	O (O^-/O^-)									C3'-endo (^3E)	OH(3') → Phos (=O)
dGMPA5	O (O^-/O^-)									C3'-endo/C2'-exo ($^3T_2$)	
dGMPA6	O (O^-/O^-)									C3'-endo (^3E)	OH(3') → Phos (=O)
dGMPA7	O (O^-/O^-)									C3'-endo/C2'-exo ($^3T_2$)	OH(3') → Phos (=O)
dGMPA8	O (=O/O^-)									C3'-endo/C2'-exo ($^3T_2$)	Phos (OH) → OH(3')
dGMPA9	O (=O/O-)									C3'-endo/C2'-exo ($^3T_2$)	Phos (OH) → OH(3')
dGMPA10	O (O^-/OH)									C2'-endo/C3'-exo ($^2T_3$)	
dGMPA11	O (=O/O^-)		O							C3'-endo/C4'-exo ($^3T_4$)	
dGMPA12	O (=O/O^-)		O							O4'-endo/C1'-exo ($^OT_1$)	
dGMPA13	O (=O/O^-)				O				O	C3'-endo/C2'-exo ($^3T_2$)	
***Syn forms*[(b)]**											
dGMPS1					O				O	C2'-endo/C1'-exo ($^2T_1$)	OH(3') → Phos (O^-)
dGMPS2	O (O^-/O^-)		O							C3'-endo/C2'-exo ($^3T_2$)	
dGMPS3	O (=O/O^-)									C3'-endo/C2'-exo ($^3T_2$)	Phos (OH) → OH(3')
dGMPS4	O (=O/O^-)		O							C3'-endo/C2'-exo ($^3T_2$)	
dGMPS5	O (=O/O^-)					O				C2'-endo/C3'-exo ($^2T_3$)	
dGMPS6	O (O^-)	O		O				O		C2'-endo/C3'-exo ($^2T_3$)	
dGMPS7	O (=O/O^-)	O						O		C3'-endo/C2'-exo ($^3T_2$)	
dGMPS8	O (O^-)				O				O	C2'-endo/C3'-exo ($^2T_3$)	Phos (OH) → O (4')
dGMPS9	O (=O/O^-)				O				O	C3'-endo/C2'-exo ($^3T_2$)	
dGMPS10	O (=O/O^-)				O				O	C3'-endo/C2'-exo ($^3T_2$)	

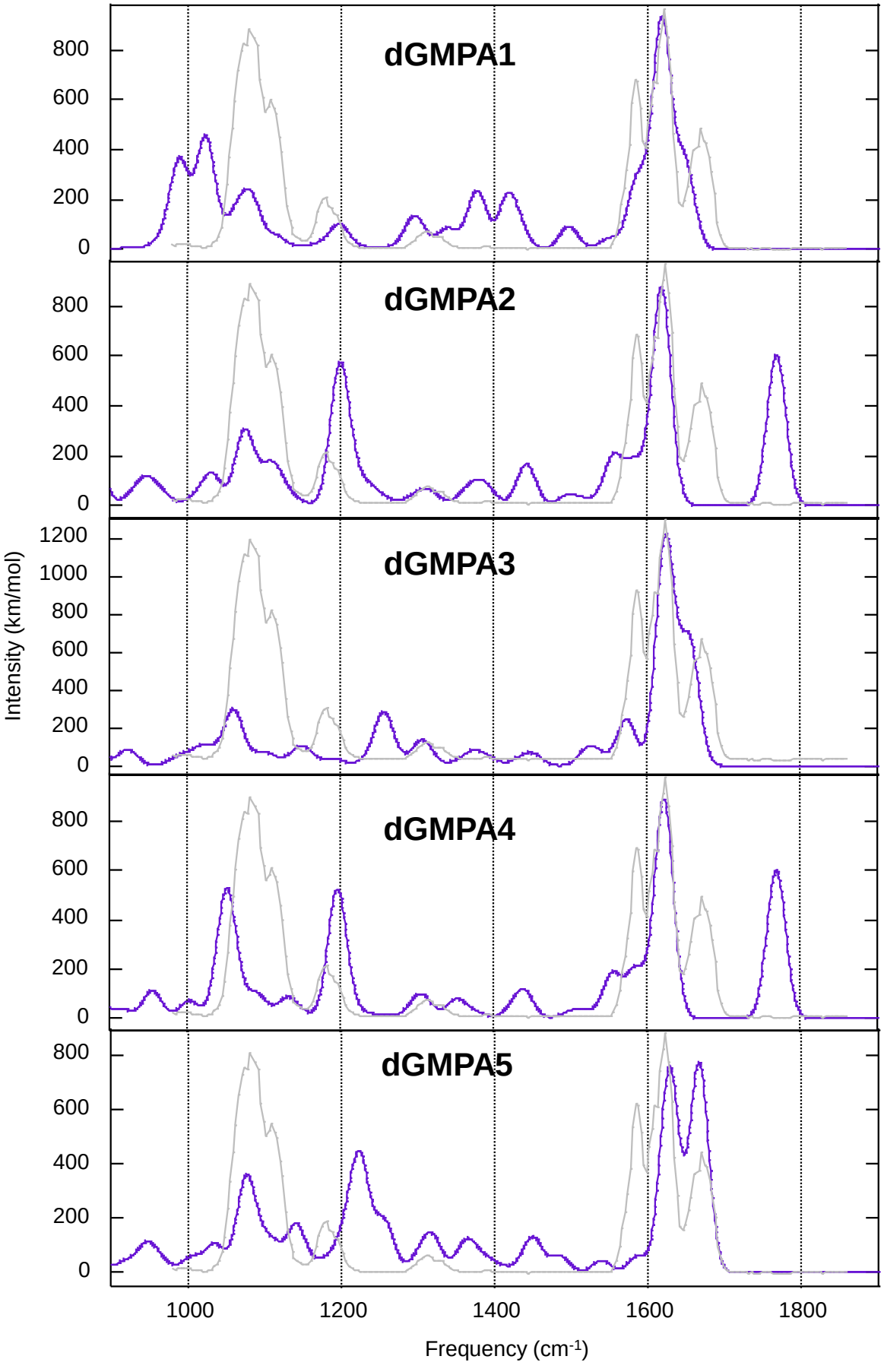
(a) Four ring atoms are considered as planar (E forms) when their associated torsional angle is greater than 179°

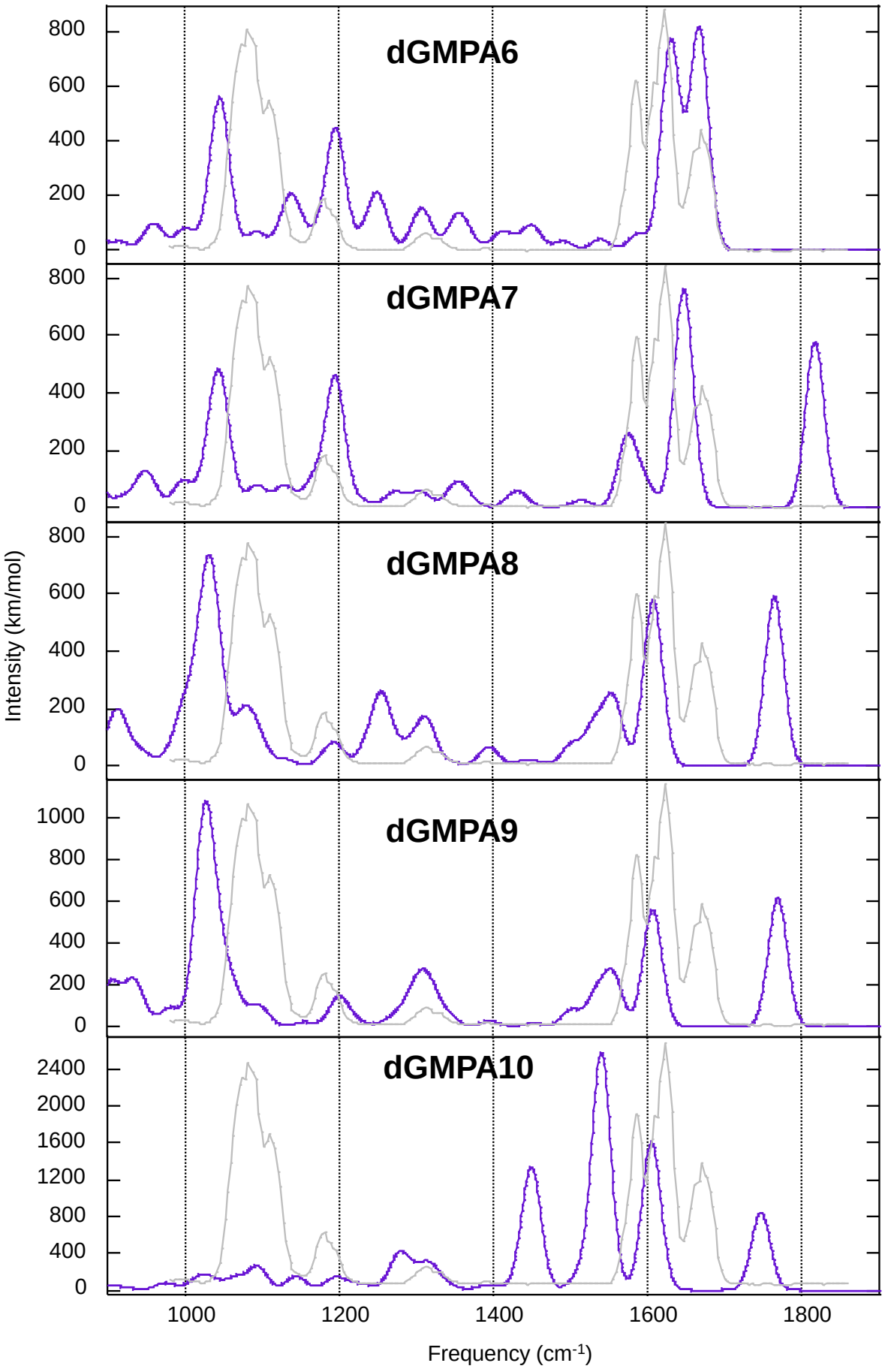
(b) By convention, the *Syn* conformation (S) corresponds to a C4-N9-C'1-O4' torsional angle ranging from 0 to ±90°. Otherwise, the conformation is *Anti* (A)

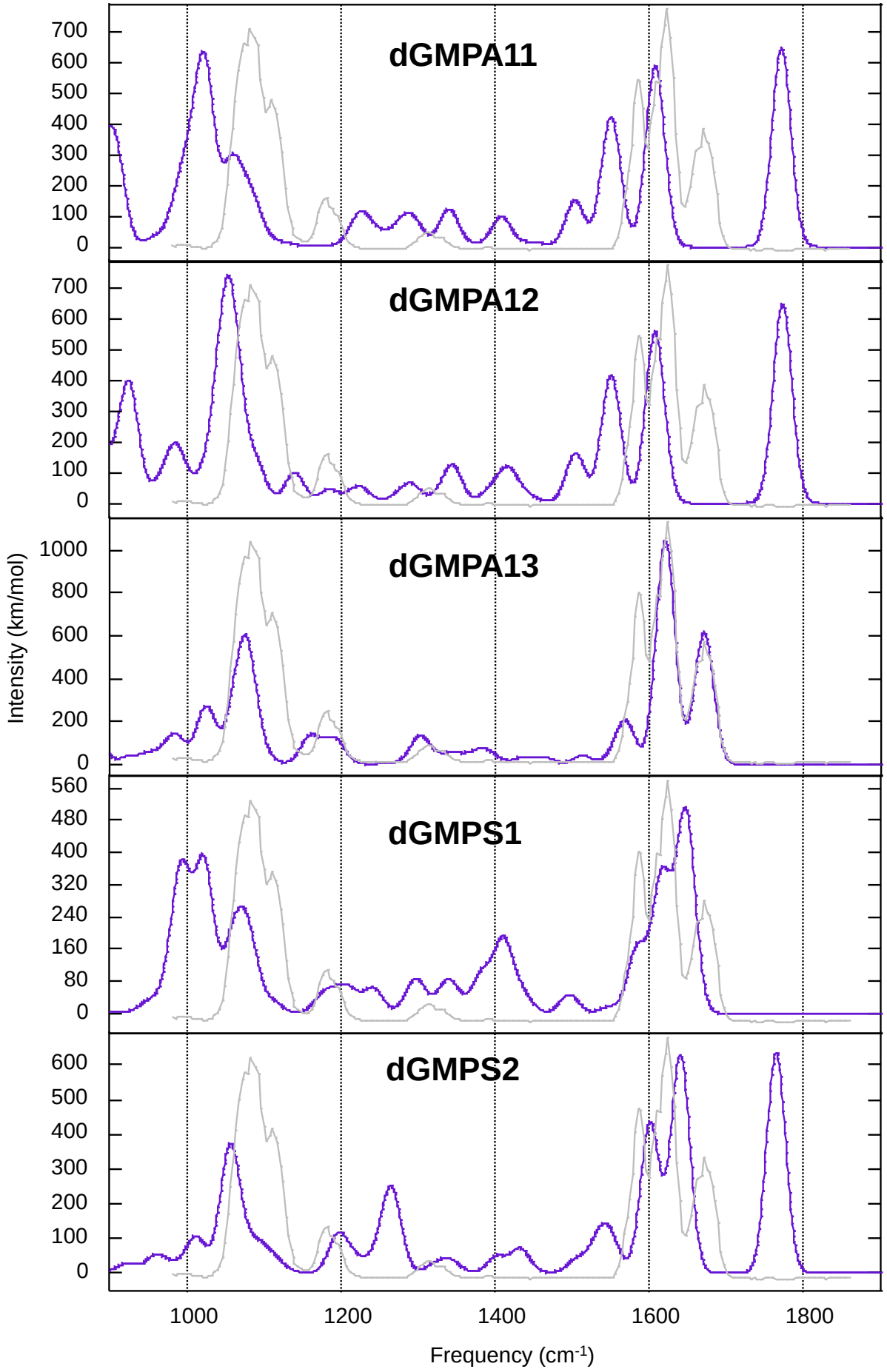
3S. Total energy, thermal correction to Gibbs free energy (TCG) and ZPE (Hartree) of the various structures considered during this study.

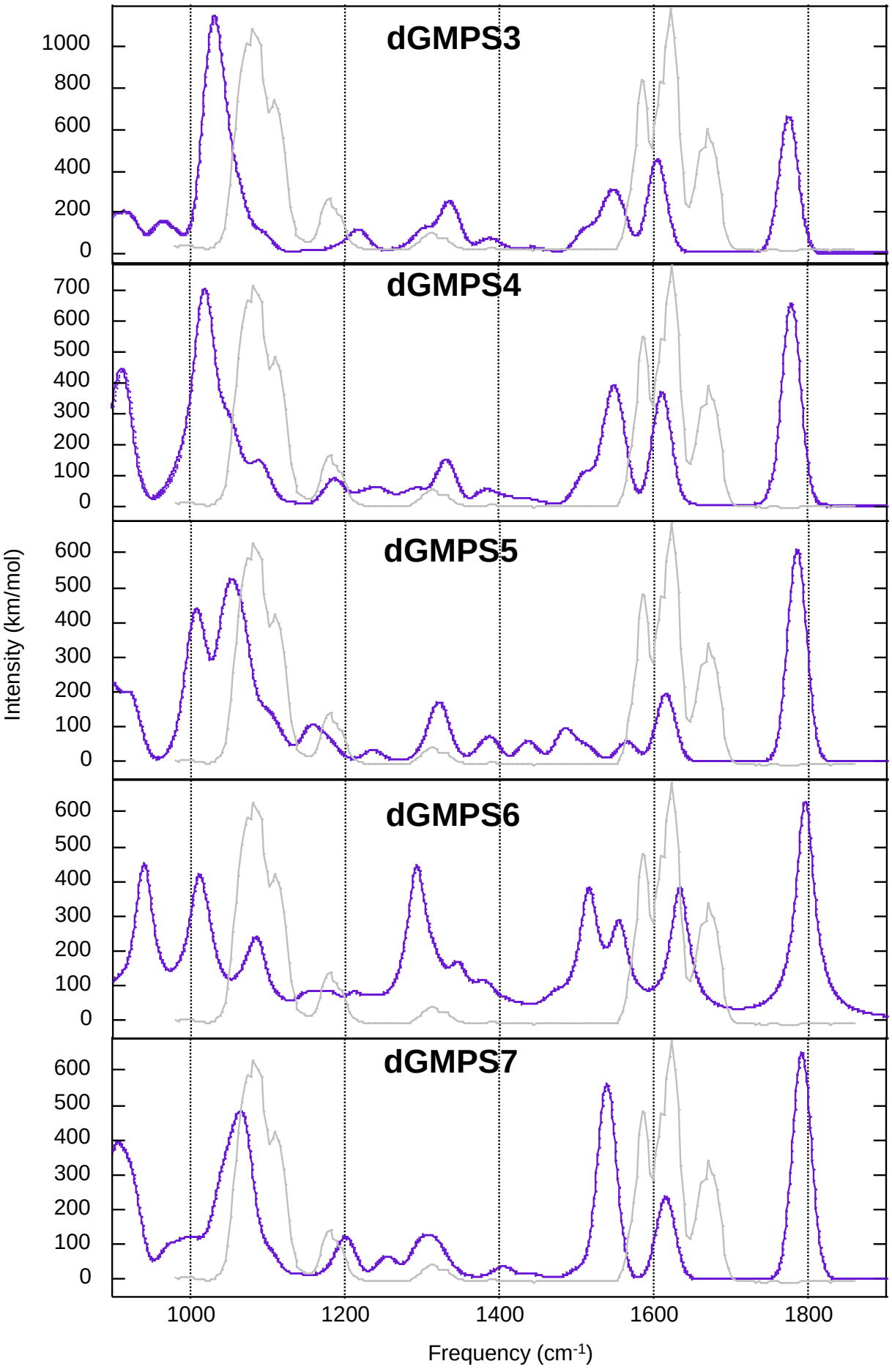
Structure	B3LYP/6-31G(d,p)			B3LYP//6-311+G(2df,2p)
	E	ZPE	TCG	E
dGMPA1	-1533.845199	0.266534	0.209900	-1534.329415
dGMPA2	-1533.956524	0.268431	0.212373	-1534.443255
dGMPA3	-1533.955654	0.267647	0.216837	-1534.434760
dGMPA4	-1533.951044	0.269049	0.212966	-1534.437542
dGMPA5	-1533.930100	0.268004	0.211968	-1534.41654
dGMPA6	-1533.93549	0.268700	0.212493	-1534.421218
dGMPA7	-1533.917473	0.267758	0.211300	-1534.404346
dGMPA8	-1533.928523	0.268243	0.213293	-1534.414012
dGMPA9	-1533.928081	0.267856	0.211509	-1534.414562
dGMPA10	-1533.881039	0.265704	0.206523	
dGMPA11	-1533.929477	0.266978	0.211334	-1534.414943
dGMPA12	-1533.93568	0.266842	0.211183	-1534.422404
dGMPA13	-1533.993128	0.268303	0.216814	-1534.475306
dGMPS1	-1533.841038	0.266733	0.210618	
dGMPS2	-1533.951487	0.269717	0.218234	-1534.431864
dGMPS3	-1533.929210	0.267705	0.212417	-1534.416566
dGMPS4	-1533.942752	0.267361	0.214402	-1534.425433
dGMPS5	-1533.928814	0.267843	0.214730	-1534.412366
dGMPS6	-1533.945020	0.267200	0.214716	-1534.424076
dGMPS7	-1533.961591	0.267712	0.215996	-1534.442794
dGMPS8	-1533.965819	0.268626	0.217449	-1534.448121
dGMPS9	-1533.987905	0.268021	0.215972	-1534.471506
dGMPS10	-1533.989783	0.267613	0.215146	-1534.474311

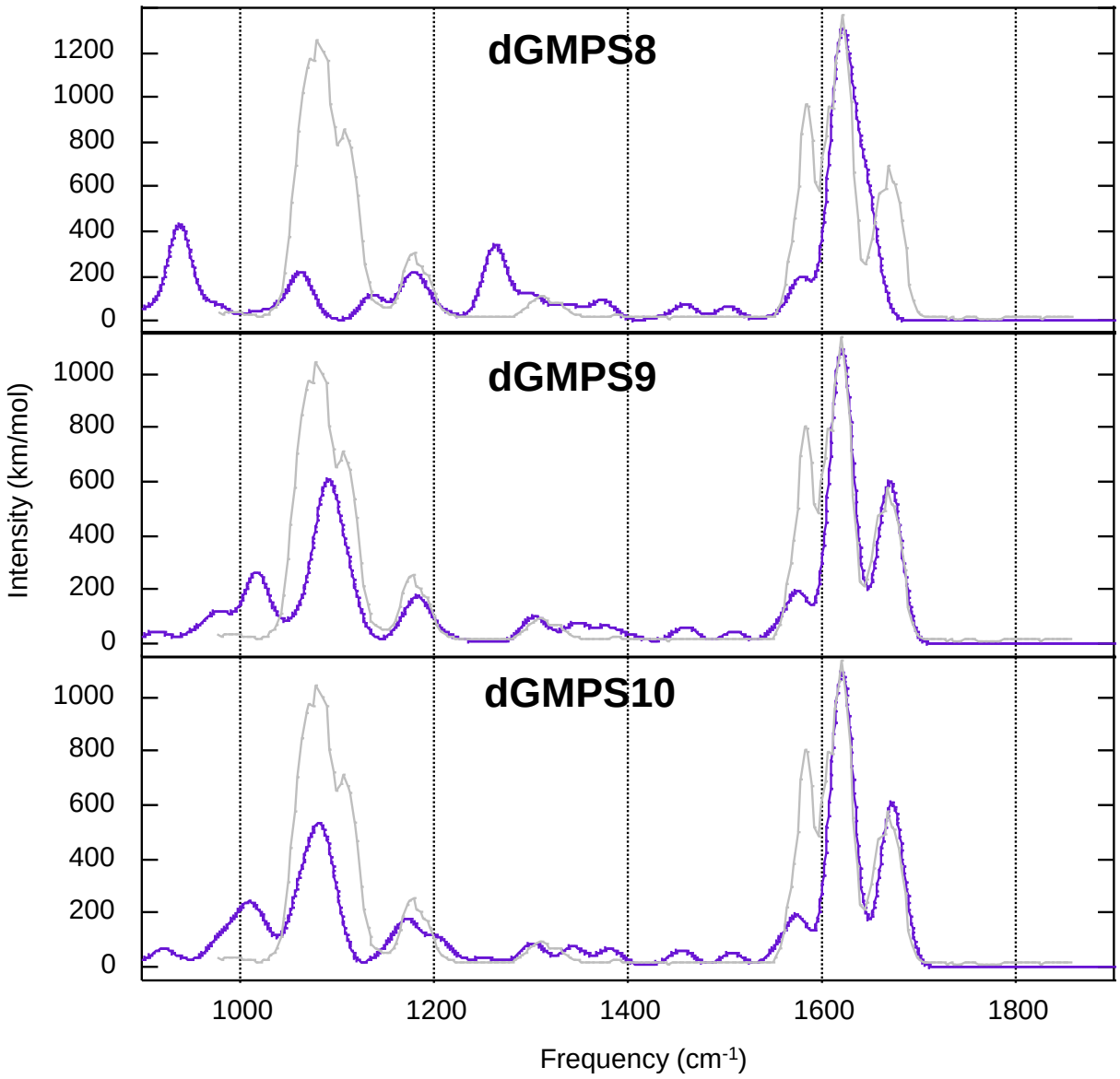
4S. DFT-computed IR absorption spectra for the [Pb(dGMP)-H]$^+$ structures. The experimental IRMPD spectrum is overlayed in grey.




dGMPA6
dGMPA7
dGMPA8
dGMPA9
dGMPA10
Intensity (km/mol)
Frequency (cm-1)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2400


dGMPA11
dGMPA12
dGMPA13
dGMPS1
dGMPS2
Intensity (km/mol)
Frequency (cm-1)
1000
1200
1400
1600
1800


dGMPS3
dGMPS4
dGMPS5
dGMPS6
dGMPS7
Intensity (km/mol)
Frequency (cm-1)
1000
1200
1400
1600
1800


dGMPS8
dGMPS9
dGMPS10
Intensity (km/mol)
Frequency (cm-1)
0
200
400
600
800
1000
1200
1400
1600
1800

5S. Evolution of [Pb(dGMP)-H]$^+$ drift time as a function of 1/E, E the electric field applied across the mobility tube. Inset shows an arrival time distribution at E = 700V/m (blue) overlaid with the predicted distribution (red) for a single conformation by the same experimental conditions. The predicted distribution for CCS 10% higher (dashed green) is well separated, showing that only one family of conformations is observed experimentally. The CCS of the [Pb(dGMP-H]$^+$ complex is determined from the slope of the line as 99.6 Å2.