Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supporting Information

A Correlated Ab Initio Quantum Chemical Study of the Interaction of the Na^+, Mg^{2+}, Ca^{2+} and Zn^{2+} Ions with the Tautomers of Cytosine in Presence of Polar Solvent

Ivan V. Rostov and Rika Kobayashi

Throughout the Electronic Supporting Information Section, the “Solvent” columns in tables and graphs show results for relative stabilities of tautomeric complexes calculated on the gas-phase geometries with addition of solvent effects (IEFPCM). The “Relaxation” data in tables and graphs were calculated with account of solvent effects as well, but on geometries equilibrated in presence of the solvent polarisation field.

Table S1. Relative stabilities (in kcal/mol) of the cytosine tautomers calculated by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Cytosine													
ωB97XD				MP2				CCSD			CCSD(T)		
	Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent		Gas-Phase	Solvent
cwc	0.0	0.0	0.0	cwc	0.0	0.0	0.0	cwc	0.0	0.0	cwc	0.0	0.0
ct1a	1.4	6.8	7.2	ct1a	-1.4	3.4	3.9	ct1a	-0.6	4.1	ct1a	-0.9	3.8
ct1b	0.7	6.7	7.1	ct1b	-1.9	3.3	3.8	ct1b	-1.1	4.2	ct1b	-1.4	3.9
ct2	7.1	5.4	5.0	ct2	7.6	5.5	5.2	ct2	7.7	6.1	ct2	7.6	6.0
ct3a	1.1	5.1	6.8	ct3a	1.1	4.8	5.3	ct3a	-0.2	3.4	ct3a	0.2	3.8
ct3b	3.0	6.4	5.5	ct3b	2.8	6.0	6.4	ct3b	1.5	4.6	ct3b	1.8	4.9
ct4a	21.5	24.4	24.8	ct4a	19.6	21.9	22.4	ct4a	18.9	21.2	ct4a	18.6	20.9
ct4b	13.7	20.4	20.9	ct4b	11.7	17.9	18.3	ct4b	10.9	17.0	ct4b	10.8	16.9
ct4c	25.6	26.1	26.5	ct4c	23.3	23.6	24.0	ct4c	22.6	22.7	ct4c	22.3	22.4
ct4d	16.8	22.0	22.4	ct4d	14.5	19.3	19.7	ct4d	13.7	18.4	ct4d	13.5	18.2
ct5a	22.4	23.5	23.8	ct5a	19.8	20.8	21.2	ct5a	18.9	19.8	ct5a	18.7	19.6
ct5b	32.5	28.5	28.1	ct5b	30.2	26.1	25.7	ct5b	29.2	25.2	ct5b	28.8	24.8
ct5c	19.1	22.5	22.8	ct5c	16.5	19.7	20.0	ct5c	15.5	18.5	ct5c	15.4	18.4
ct5d	28.4	27.3	26.9	ct5d	26.1	24.8	24.4	ct5d	24.9	23.6	ct5d	24.7	23.4

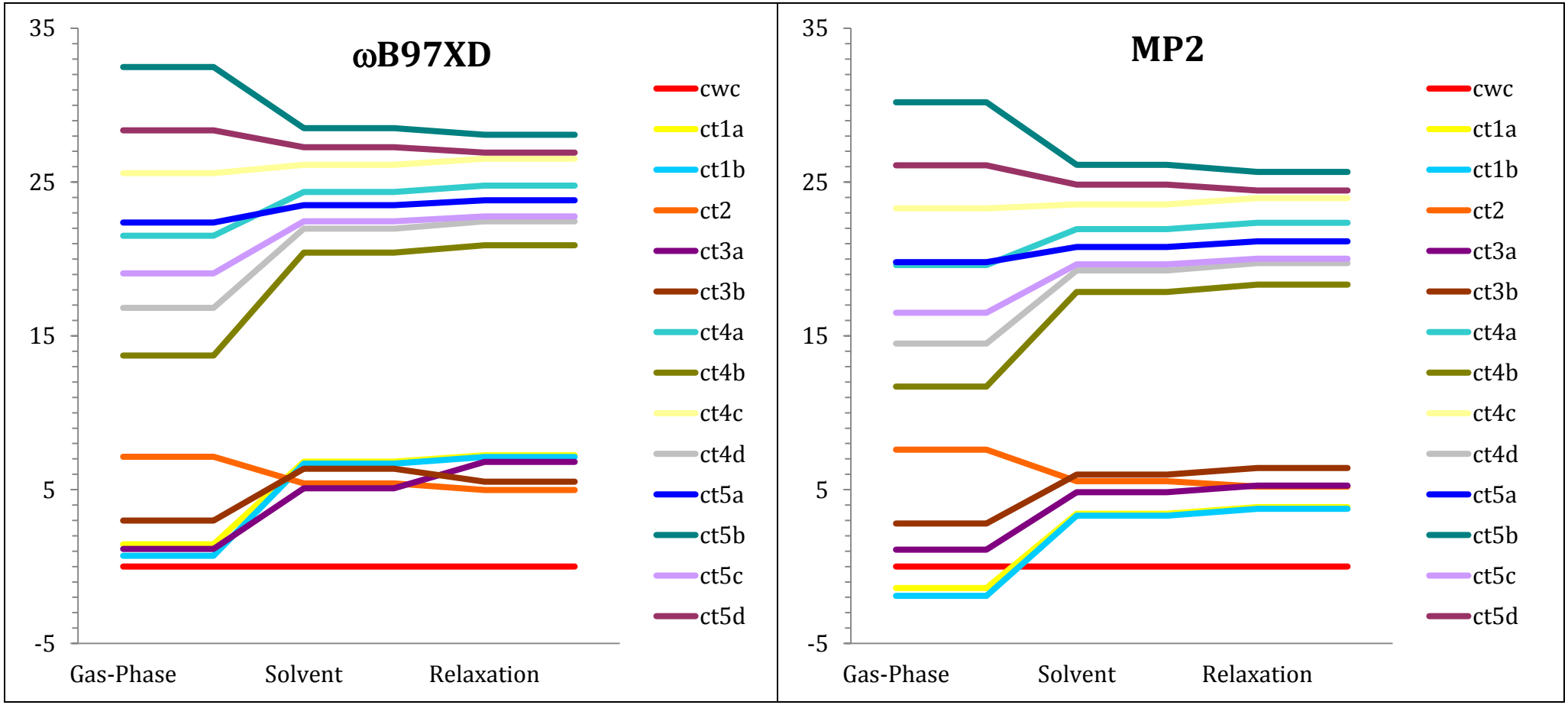
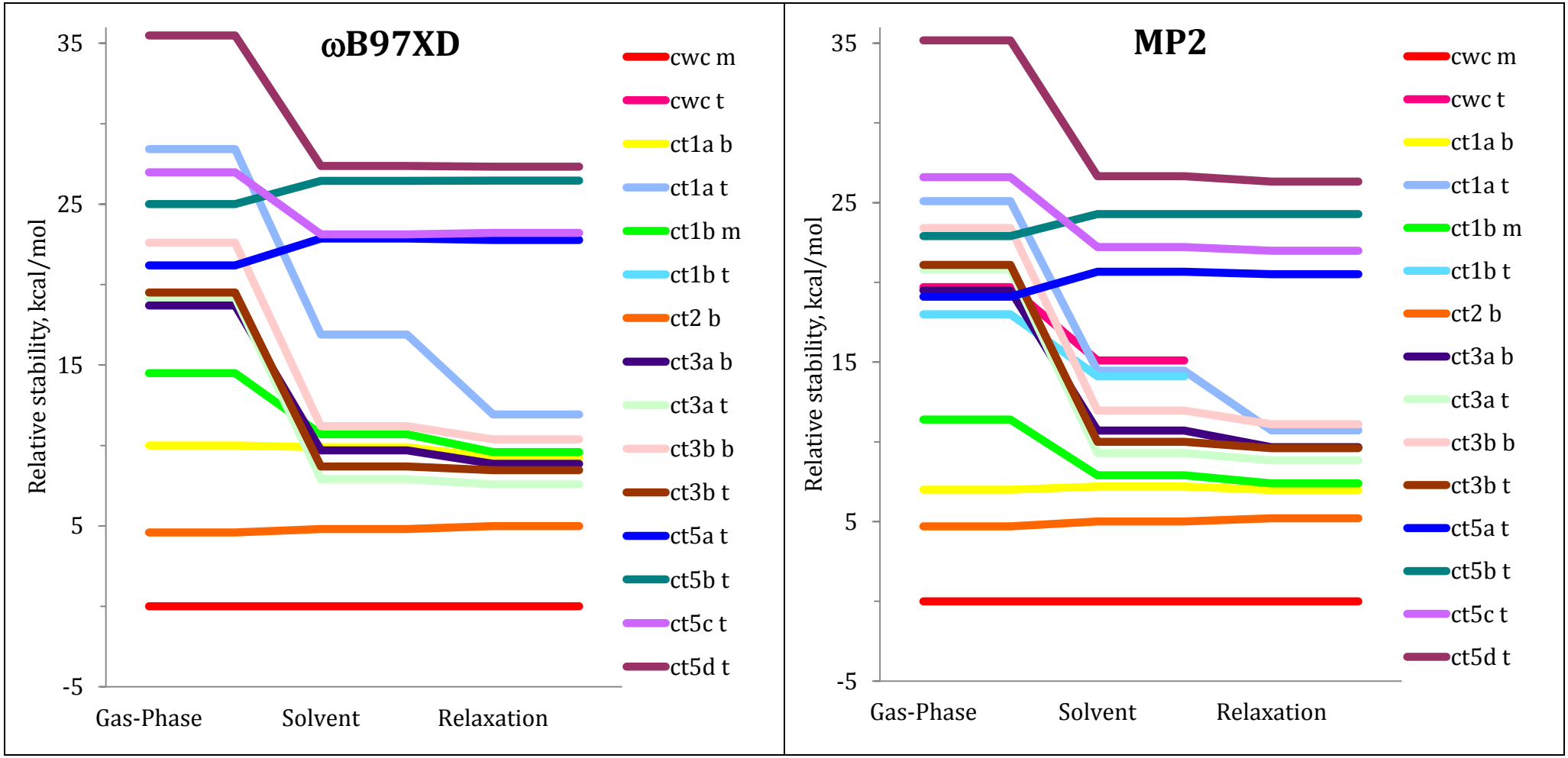


Fig. S1 Relative stabilities (in kcal/mol) of the cytosine tautomers calculated by the ωB97XD and MP2 methods.

Table S2. Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Na^+ by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Na^+													
ωB97XD				MP2				CCSD			CCSD(T)		
	Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent		Gas-Phase	Solvent
cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	cwc m	0.0	0.0
cwc t	–	–	–	cwc t	19.7	15.1	–	cwc t	20.5	16.0	cwc t	19.6	15.1
ct1a b	10.0	9.9	9.3	ct1a b	7.0	7.2	7.0	ct1a b	8.2	8.5	ct1a b	7.8	8.0
ct1a t	28.4	16.9	11.9	ct1a t	25.1	14.5	10.7	ct1a t	26.8	16.2	ct1a t	25.8	15.2
ct1b m	14.5	10.7	9.6	ct1b m	11.4	7.9	7.4	ct1b m	12.6	9.2	ct1b m	12.1	8.7
ct1b t	–	–	–	ct1b t	18.0	14.1	–	ct1b t	19.6	15.7	ct1b t	18.7	14.8
ct2 b	4.6	4.8	5.0	ct2 b	4.7	5.0	5.2	ct2 b	5.1	5.4	ct2 b	4.9	5.1
ct3a b	18.7	9.7	8.9	ct3a b	19.5	10.7	9.7	ct3a b	18.1	9.3	ct3a b	18.6	9.8
ct3a t	19.2	7.9	7.6	ct3a t	20.8	9.3	8.8	ct3a t	20.5	9.1	ct3a t	20.6	9.1
ct3b b	22.6	11.2	10.4	ct3b b	23.4	12.0	11.1	ct3b b	21.9	10.5	ct3b b	22.3	10.9
ct3b t	19.5	8.7	8.5	ct3b t	21.1	10.0	9.6	ct3b t	20.8	9.8	ct3b t	20.8	9.8
ct5a t	21.2	22.9	22.8	ct5a t	19.1	20.7	20.5	ct5a t	18.8	20.3	ct5a t	18.5	20.1
ct5b t	25.0	26.5	26.5	ct5b t	22.9	24.3	24.3	ct5b t	22.5	23.9	ct5b t	22.2	23.6
ct5c t	27.0	23.1	23.2	ct5c t	26.6	22.2	22.0	ct5c t	26.6	22.3	ct5c t	26.4	22.0
ct5d t	35.5	27.4	27.3	ct5d t	35.2	26.7	26.3	ct5d t	35.3	26.7	ct5d t	34.8	26.3



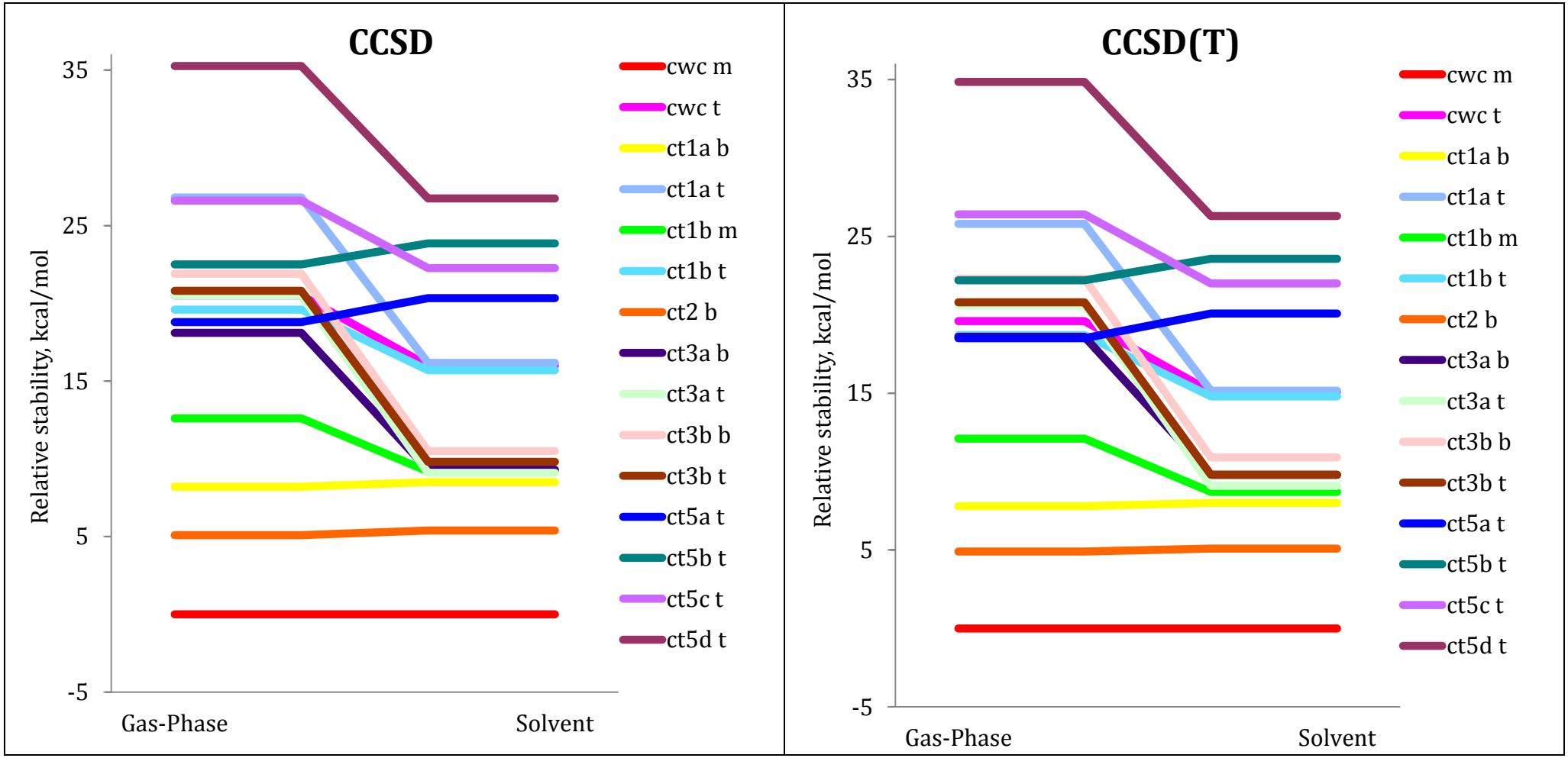
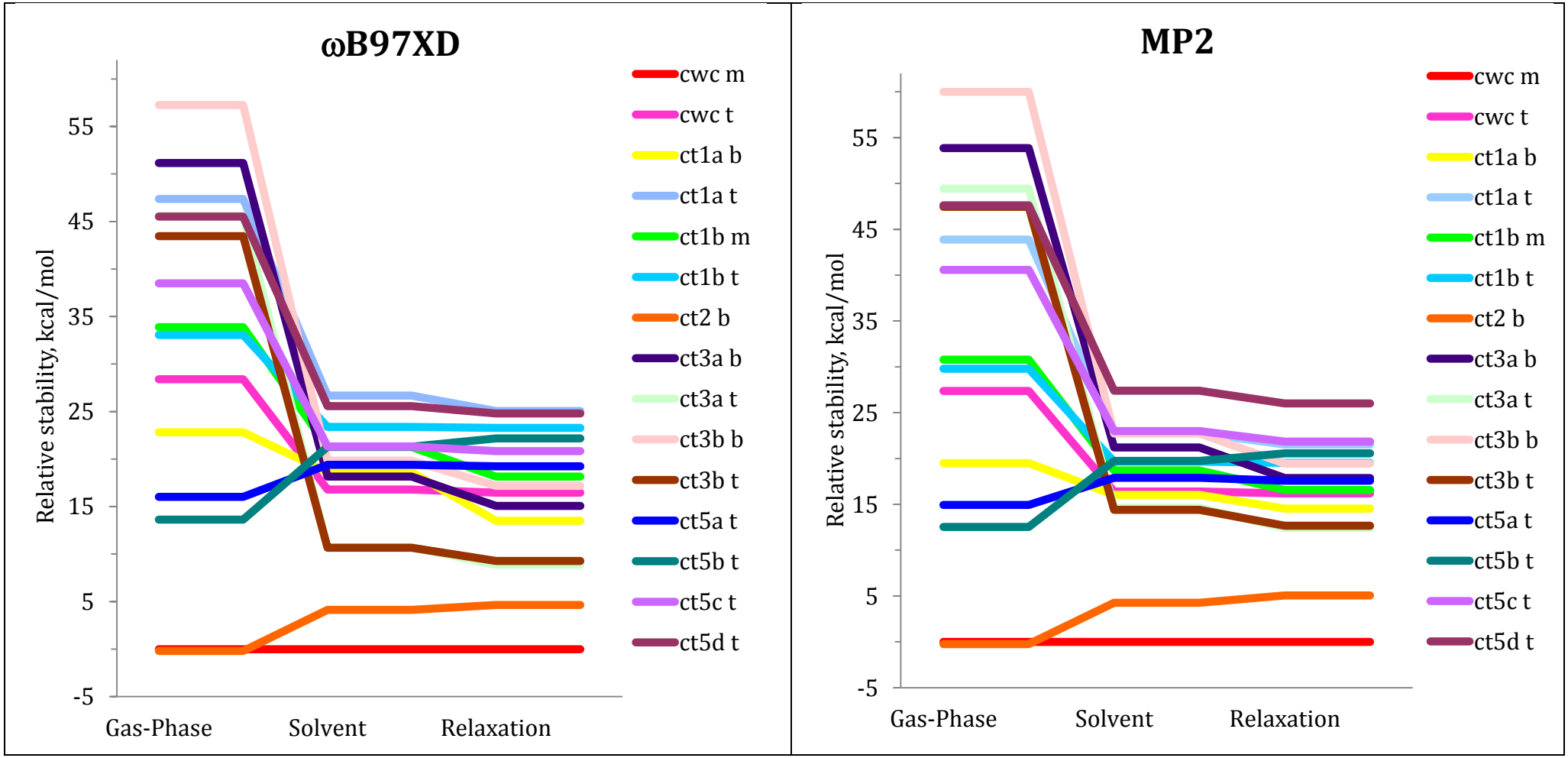


Fig. S2 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Na^+ by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Table S3 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Mg^{2+} by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Mg^{2+}												
ωB97XD				MP2				CCSD			CCSD(T)		
	Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent		Gas-Phase	Solvent
cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	cwc m	0.0	0.0
cwc t	28.4	16.8	16.5	cwc t	27.4	16.4	16.2	cwc t	29.2	18.3	cwc t	28.0	17.0
ct1a b	22.8	18.6	13.5	ct1a b	19.5	16.0	14.5	ct1a b	21.3	17.8	ct1a b	20.7	17.2
ct1a t	47.4	26.7	25.1	ct1a t	43.9	22.8	21.5	ct1a t	46.3	25.2	ct1a t	44.9	23.8
ct1b m	33.9	21.3	18.2	ct1b m	30.8	18.7	16.6	ct1b m	32.6	20.5	ct1b m	31.9	19.8
ct1b t	33.1	23.4	23.3	ct1b t	29.8	19.6	19.5	ct1b t	32.0	21.9	ct1b t	30.9	20.8
ct2 b	-0.2	4.1	4.7	ct2 b	-0.2	4.3	5.1	ct2 b	0.0	4.5	ct2 b	-0.1	4.4
ct3a b	51.1	18.2	15.1	ct3a b	53.9	21.2	17.9	ct3a b	52.7	20.1	ct3a b	53.1	20.5
ct3a t	45.6	10.7	8.9	ct3a t	49.4	14.6	12.4	ct3a t	50.5	15.7	ct3a t	50.1	15.3
ct3b b	57.3	19.8	17.2	ct3b b	60.0	22.7	19.4	ct3b b	58.8	21.5	ct3b b	59.1	21.8
ct3b t	43.5	10.7	9.3	ct3b t	47.4	14.4	12.7	ct3b t	48.3	15.2	ct3b t	47.9	14.9
ct5a t	16.0	19.4	19.2	ct5a t	14.9	17.9	17.6	ct5a t	15.2	18.1	ct5a t	14.9	17.8
ct5b t	13.6	21.3	22.2	ct5b t	12.5	19.7	20.6	ct5b t	12.6	19.8	ct5b t	12.4	19.6
ct5c t	38.5	21.3	20.8	ct5c t	40.6	23.0	21.8	ct5c t	41.8	24.3	ct5c t	41.4	23.8
ct5d t	45.5	25.6	24.8	ct5d t	47.6	27.4	26.0	ct5d t	49.0	28.8	ct5d t	48.5	28.2



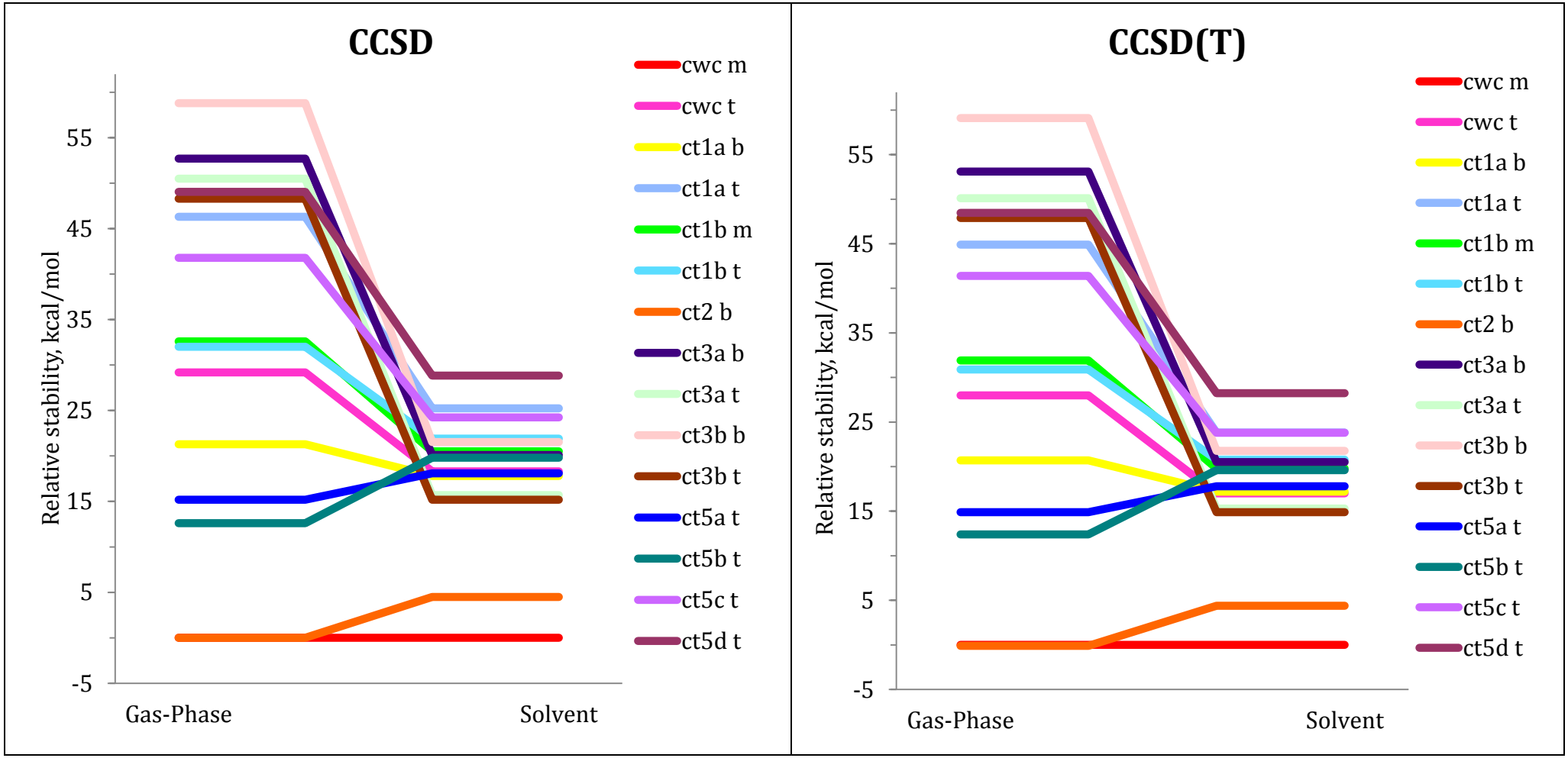
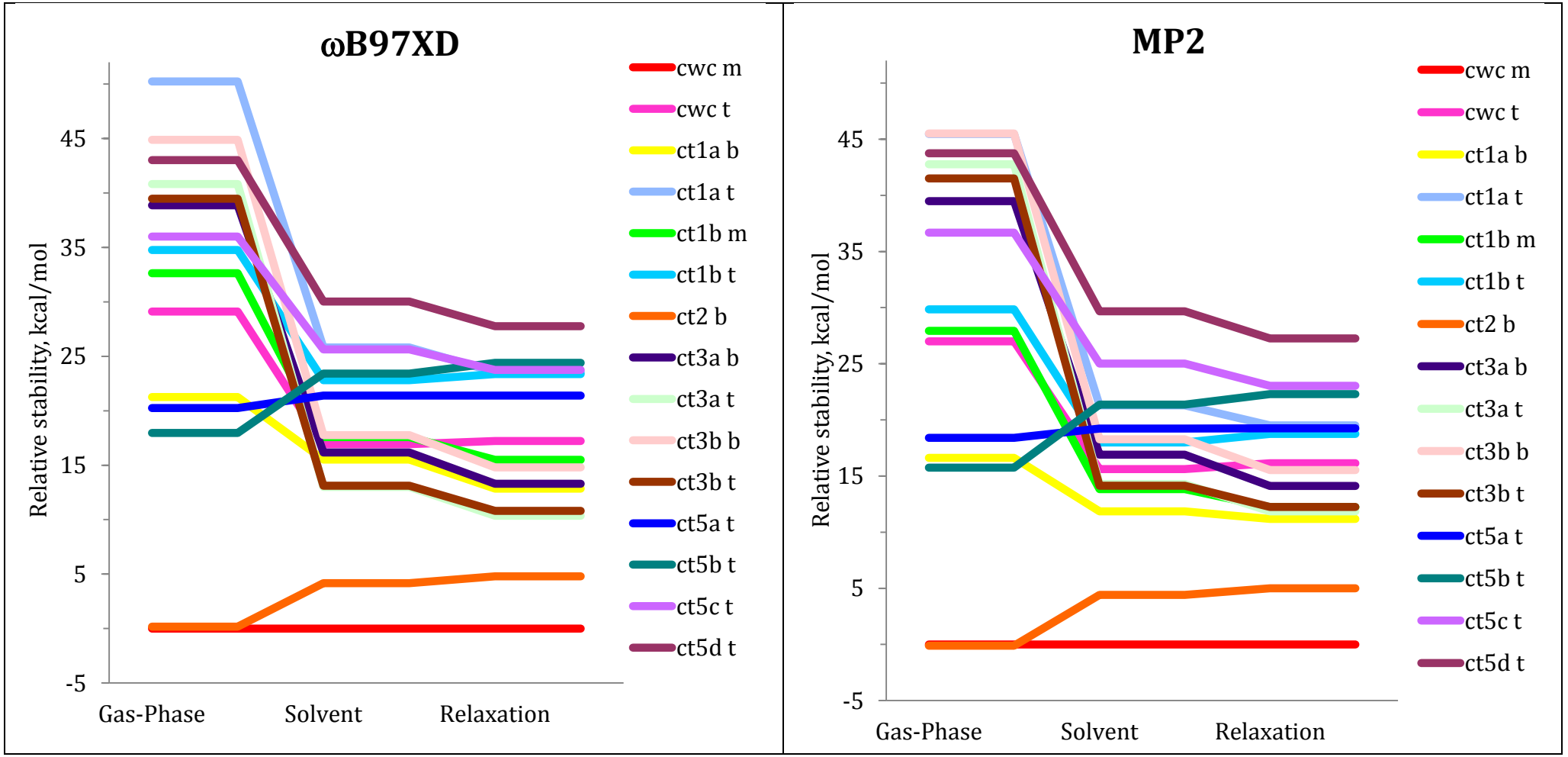


Fig. S3 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Mg^{2+} by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Table S4 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Ca^{2+} by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Ca^{2+}												
ωB97XD				MP2				CCSD			CCSD(T)		
	Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent	Relaxation		Gas-Phase	Solvent		Gas-Phase	Solvent
cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	cwc m	0.0	0.0
cwc t	29.1	16.9	17.2	cwc t	27.0	15.6	16.1	cwc t	28.3	16.9	cwc t	27.3	15.9
ct1a b	21.2	15.5	12.9	ct1a b	16.6	11.8	11.2	ct1a b	18.1	13.4	ct1a b	17.6	12.9
ct1a t	50.3	25.8	23.5	ct1a t	45.5	21.3	19.5	ct1a t	47.7	23.5	ct1a t	46.4	22.2
ct1b m	32.6	17.6	15.5	ct1b m	27.9	13.8	12.2	ct1b m	29.5	15.4	ct1b m	28.9	14.8
ct1b t	34.8	22.8	23.4	ct1b t	29.9	18.0	18.7	ct1b t	31.7	19.9	ct1b t	30.8	18.9
ct2 b	0.2	4.2	4.8	ct2 b	-0.1	4.4	5.0	ct2 b	0.2	4.7	ct2 b	0.1	4.6
ct3a b	38.9	16.2	13.3	ct3a b	39.5	16.9	14.1	ct3a b	37.8	15.2	ct3a b	38.2	15.6
ct3a t	40.8	13.0	10.3	ct3a t	42.8	14.3	11.9	ct3a t	43.0	14.5	ct3a t	42.8	14.3
ct3b b	44.9	17.8	14.8	ct3b b	45.5	18.3	15.5	ct3b b	43.8	16.5	ct3b b	44.0	16.7
ct3b t	39.5	13.1	10.8	ct3b t	41.5	14.1	12.2	ct3b t	41.5	14.2	ct3b t	41.4	14.0
ct5a t	20.3	21.4	21.4	ct5a t	18.4	19.2	19.2	ct5a t	18.6	19.5	ct5a t	18.4	19.2
ct5b t	18.0	23.4	24.4	ct5b t	15.7	21.4	22.3	ct5b t	15.8	21.4	ct5b t	15.6	21.3
ct5c t	36.0	25.6	23.7	ct5c t	36.7	25.0	23.0	ct5c t	37.2	25.6	ct5c t	36.9	25.3
ct5d t	43.0	30.0	27.8	ct5d t	43.8	29.7	27.3	ct5d t	44.5	30.4	ct5d t	44.0	30.4


ωB97XD
Relative stability, kcal/mol
45
35
25
15
5
-5
Gas-Phase
Solvent
Relaxation
cwc m
cwc t
ct1a b
ct1a t
ct1b m
ct1b t
ct2 b
ct3a b
ct3a t
ct3b b
ct3b t
ct5a t
ct5b t
ct5c t
ct5d t
MP2
Relative stability, kcal/mol
45
35
25
15
5
-5
Gas-Phase
Solvent
Relaxation
cwc m
cwc t
ct1a b
ct1a t
ct1b m
ct1b t
ct2 b
ct3a b
ct3a t
ct3b b
ct3b t
ct5a t
ct5b t
ct5c t
ct5d t

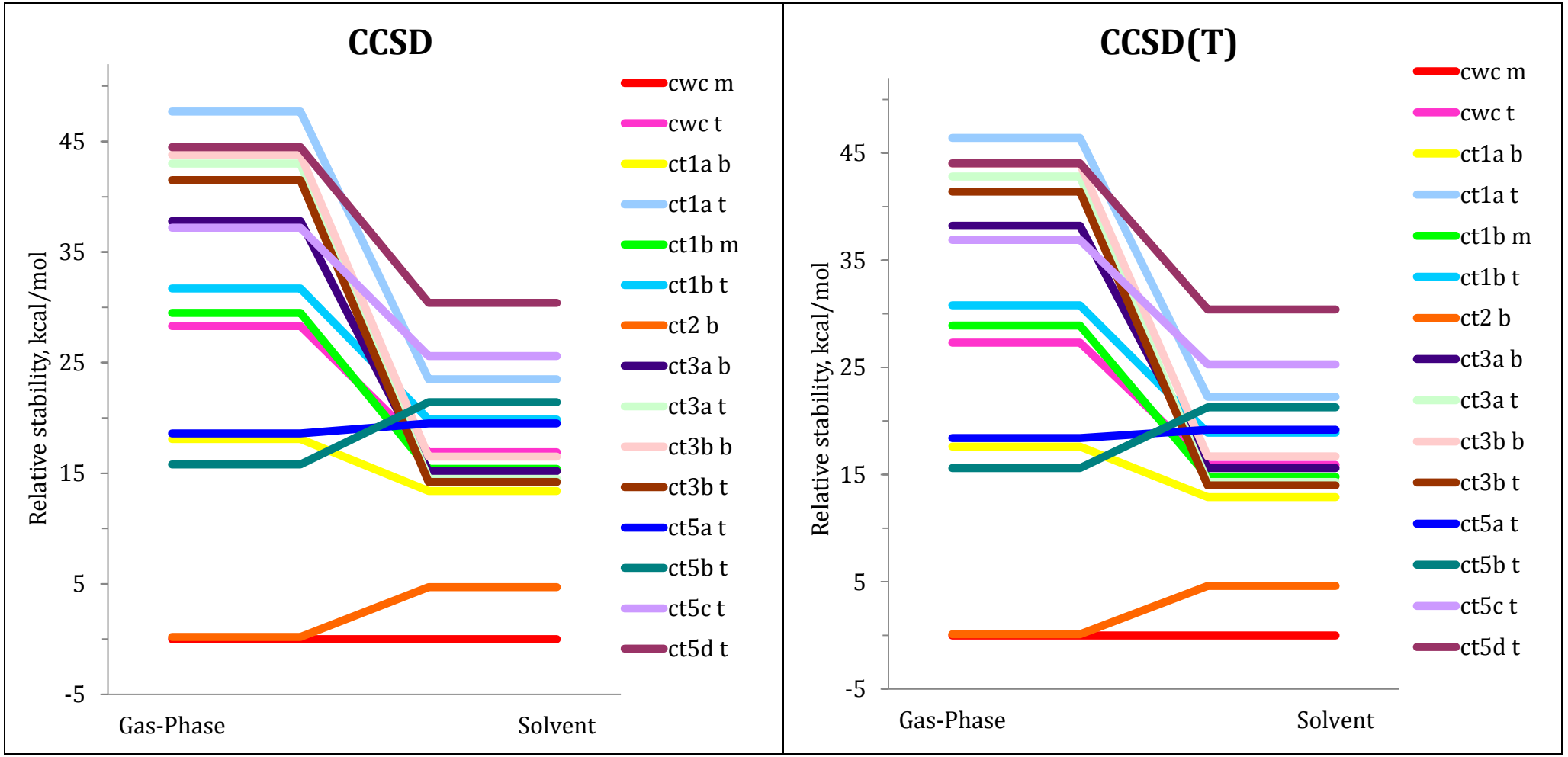
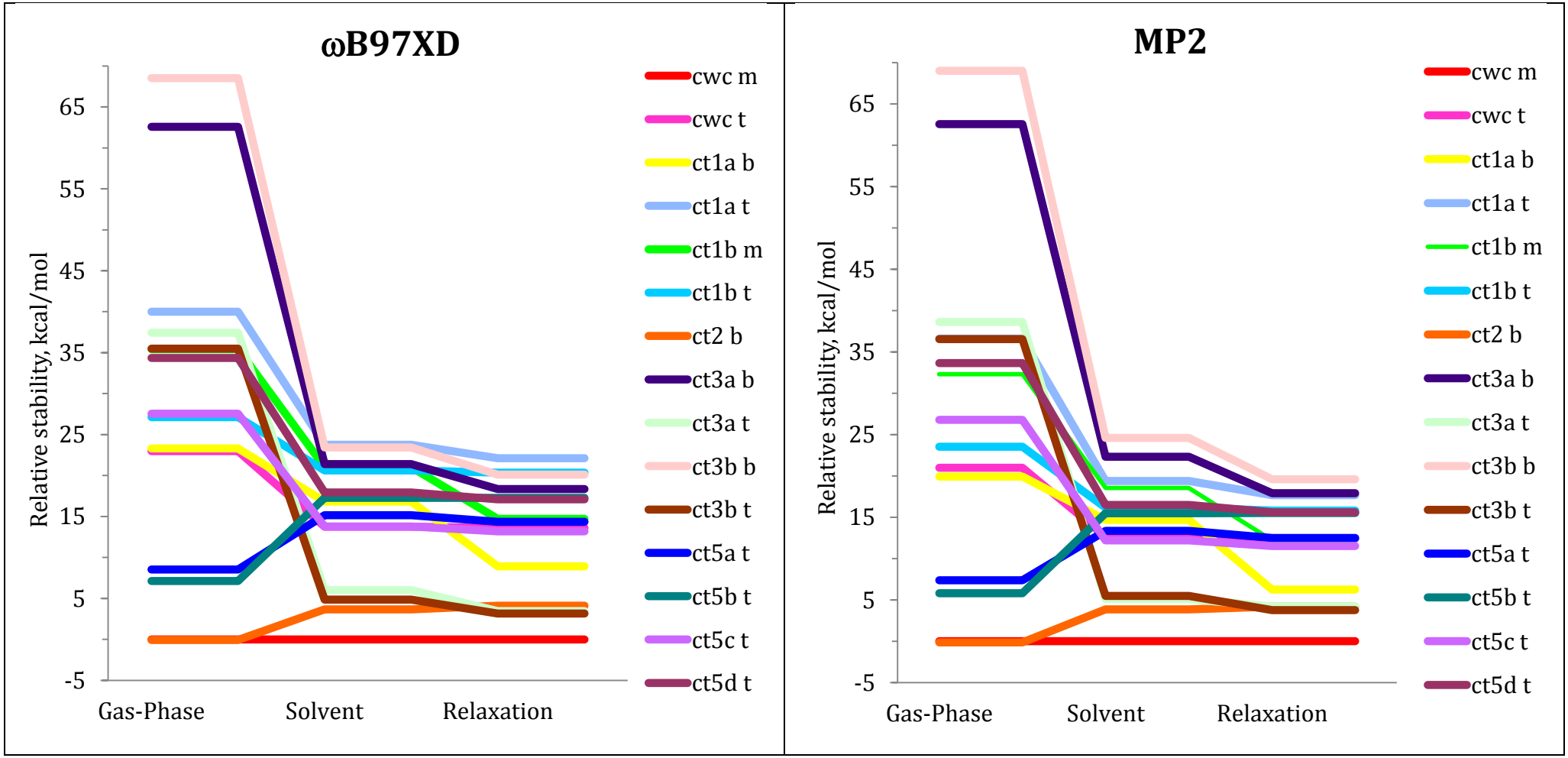


Fig. S4 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Ca^{2+} by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Table S5 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Zn^{2+} by the ωB97XD, MP2, CCSD and CCSD(T) methods.

Zn^{2+}												
ωB97XD				**MP2**				**CCSD**			**CCSD(T)**		
	Gas-Phase	**Solvent**	**Relaxation**		**Gas-Phase**	**Solvent**	**Relaxation**		**Gas-Phase**	**Solvent**		**Gas-Phase**	**Solvent**
cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	0.0	cwc m	0.0	0.0	cwc m	0.0	0.0
cwc t	23.0	13.8	13.6	cwc t	21.0	12.6	12.4	cwc t	23.5	15.1	cwc t	22.2	13.8
ct1a b	23.3	16.8	8.9	ct1a b	19.9	14.7	6.2	ct1a b	21.4	16.1	ct1a b	21.2	16.0
ct1a t	40.0	23.7	22.1	ct1a t	36.6	19.4	17.7	ct1a t	39.6	22.4	ct1a t	38.1	20.9
ct1b m	35.4	21.0	14.7	ct1b m	32.3	18.6	12.2	ct1b m	33.8	20.0	ct1b m	33.5	19.7
ct1b t	27.1	20.6	20.3	ct1b t	23.5	16.2	15.8	ct1b t	26.2	18.9	ct1b t	25.1	17.8
ct2 b	-0.1	3.7	4.1	ct2 b	-0.1	3.9	4.2	ct2 b	0.1	4.1	ct2 b	0.0	4.0
ct3a b	62.6	21.4	18.4	ct3a b	62.6	22.3	17.9	ct3a b	60.2	20.0	ct3a b	61.0	20.8
ct3a t	37.4	6.0	3.4	ct3a t	38.6	5.1	4.2	ct3a t	39.9	6.4	ct3a t	40.0	6.5
ct3b b	68.5	23.4	20.1	ct3b b	69.0	24.6	19.6	ct3b b	66.5	22.1	ct3b b	67.0	22.6
ct3b t	35.5	4.9	3.1	ct3b t	36.5	5.5	3.8	ct3b t	37.6	6.5	ct3b t	37.7	6.6
ct5a t	8.5	15.1	14.4	ct5a t	7.4	13.3	12.5	ct5a t	8.7	14.6	ct5a t	8.3	14.3
ct5b t	7.1	17.3	17.3	ct5b t	5.8	15.5	15.5	ct5b t	6.8	16.5	ct5b t	6.6	16.3
ct5c t	27.5	13.8	13.2	ct5c t	26.8	12.2	11.5	ct5c t	28.6	14.0	ct5c t	28.6	14.0
ct5d t	34.3	17.9	17.1	ct5d t	33.6	16.5	15.6	ct5d t	35.7	18.5	ct5d t	35.5	18.3


ωB97XD
MP2
Relative stability, kcal/mol
65
55
45
35
25
15
5
-5
Gas-Phase
Solvent
Relaxation
cwc m
cwc t
ct1a b
ct1a t
ct1b m
ct1b t
ct2 b
ct3a b
ct3a t
ct3b b
ct3b t
ct5a t
ct5b t
ct5c t
ct5d t

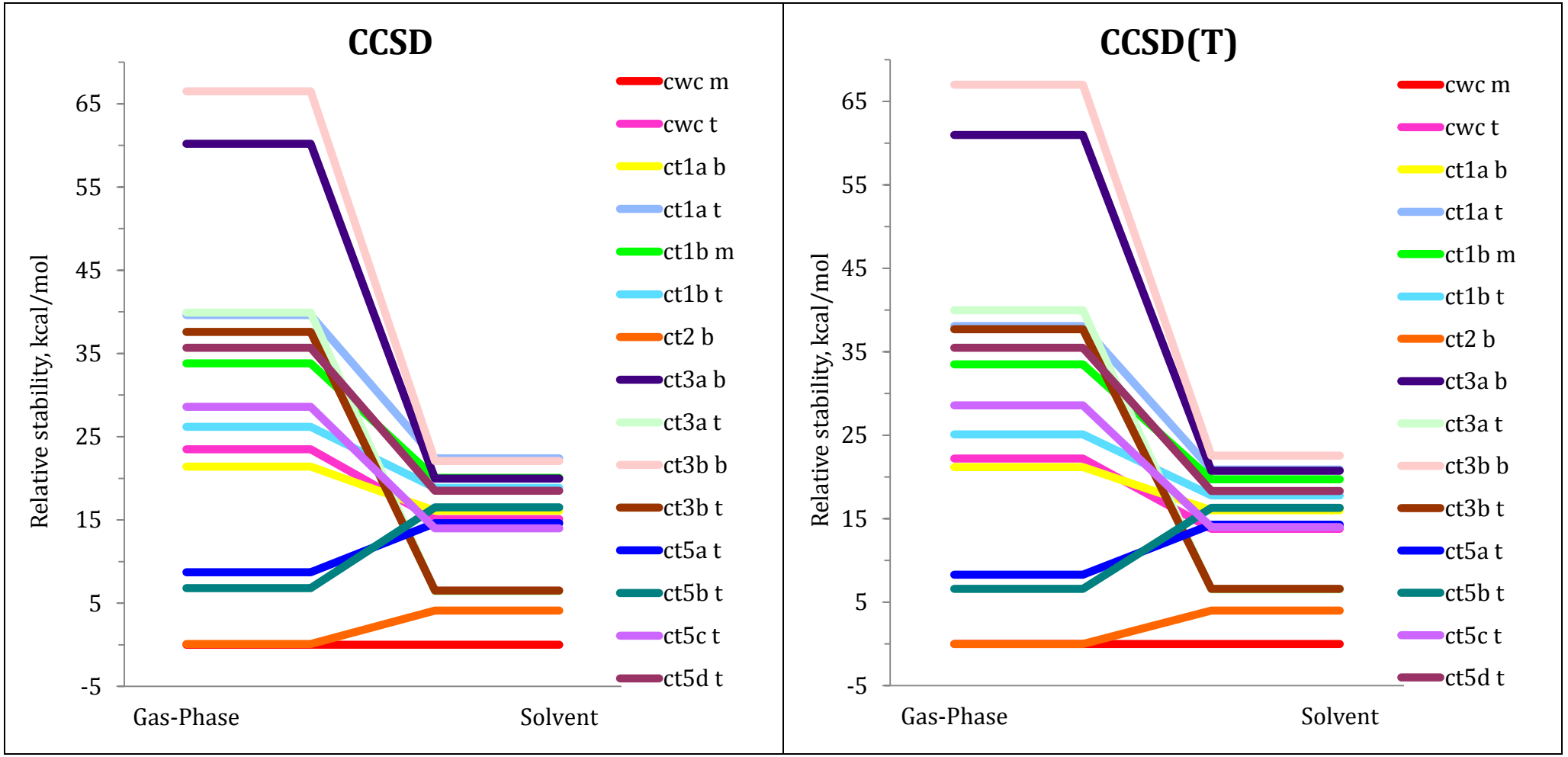


Fig. S5 Relative stabilities (in kcal/mol) of the cytosine tautomers binding with Zn^{2+} by the ωB97XD, MP2, CCSD and CCSD(T) methods.