Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Table 1S Interaction energy (kcal/mol) of Mg^{2+} and benzene complex calculated at MP2/aug-cc-pVTZ, PM3/MMpol and PM3/MM levels of theory

R (Å)	MP2	QM/MMpol			QM/MM	
	E_{inter}	E_{inter}	$E_{QM/MMpol}^{el,q'}$	$E_{QM/MMpol}^{el,\mu}$	E_{inter}	$E_{QM/MM}^{el,q}$
1.40	-69.3	-16.1	-37.6	-88.3	-0.1	-41.0
1.50	-87.6	-45.0	-36.1	-76.7	-15.8	-39.5
1.60	-100.7	-60.1	-34.5	-66.6	-24.9	-37.9
1.70	-109.3	-66.7	-33.0	-57.8	-29.9	-36.4
1.80	-114.3	-68.2	-31.5	-50.3	-32.2	-34.8
1.90	-116.5	-66.7	-30.0	-43.9	-32.9	-33.3
2.00	-116.4	-63.6	-28.6	-38.3	-32.6	-31.7
2.10	-114.5	-59.8	-27.2	-33.6	-31.7	-30.2
2.20	-111.4	-55.7	-25.9	-29.5	-30.5	-28.8
2.30	-107.3	-51.6	-24.5	-26.0	-29.1	-27.4
2.40	-102.6	-47.7	-23.3	-23.0	-27.7	-26.0
2.50	-97.5	-44.0	-22.1	-20.4	-26.3	-24.7
2.60	-92.2	-40.6	-21.0	-18.1	-24.9	-23.5
2.70	-86.7	-37.5	-19.9	-16.2	-23.5	-22.3
2.80	-81.3	-34.6	-18.8	-14.5	-22.2	-21.1
2.90	-76.0	-32.0	-17.8	-13.0	-21.0	-20.0
3.00	-70.9	-29.7	-16.9	-11.7	-19.9	-19.0
3.10	-65.9	-27.5	-16.0	-10.5	-18.8	-18.0
3.20	-61.2	-25.6	-15.2	-9.5	-17.7	-17.1
3.30	-56.8	-23.8	-14.4	-8.6	-16.8	-16.2
3.40	-52.6	-22.2	-13.6	-7.9	-15.9	-15.4

3.60	-45.0	-19.3	-12.3	-6.5	-14.2	-13.8
3.80	-38.4	-16.9	-11.1	-5.5	-12.8	-12.5
4.00	-32.7	-14.9	-10.0	-4.6	-11.5	-11.3
4.50	-22.2	-11.1	-7.8	-3.1	-8.9	-8.8
5.00	-15.4	-8.4	-6.1	-2.2	-7.0	-6.9

Table 2S Interaction energy (kcal/mol) of Li^+ and benzene complex calculated at MP2/aug-cc-pVTZ, MNDO/MMpol and MNDO/MM levels of theory

R (Å)	MP2	QM/MMpol			QM/MM	
	E_{inter}	E_{inter}	$E^{el,q'}_{QM/MMpol}$	$E^{el,\boldsymbol{\mu}}_{QM/MMpol}$	E_{inter}	$E^{el,q}_{QM/MM}$
1.40	-21.9	-4.3	-18.0	-27.4	13.4	-19.5
1.50	-27.8	-15.0	-17.3	-23.6	1.8	-18.7
1.60	-31.8	-20.7	-16.6	-20.3	-5.3	-18.0
1.70	-34.3	-23.4	-15.8	-17.5	-9.6	-17.3
1.80	-35.6	-24.2	-15.1	-15.1	-12.0	-16.5
1.90	-35.9	-23.9	-14.4	-13.0	-13.2	-15.8
2.00	-35.4	-23.0	-13.7	-11.3	-13.7	-15.1
2.10	-34.5	-21.8	-13.0	-9.8	-13.7	-14.4
2.20	-33.1	-20.4	-12.4	-8.5	-13.5	-13.7
2.30	-31.6	-19.1	-11.8	-7.5	-13.1	-13.1
2.40	-29.8	-17.8	-11.2	-6.5	-12.6	-12.4
2.50	-28.0	-16.5	-10.6	-5.8	-12.0	-11.8
2.60	-26.2	-15.4	-10.1	-5.1	-11.5	-11.2
2.70	-24.4	-14.3	-9.5	-4.5	-10.9	-10.6
2.80	-22.6	-13.3	-9.0	-4.0	-10.4	-10.1
2.90	-20.9	-12.4	-8.6	-3.6	-9.8	-9.6
3.00	-19.3	-11.5	-8.1	-3.2	-9.3	-9.1
3.10	-17.8	-10.8	-7.7	-2.9	-8.8	-8.6
3.20	-16.4	-10.1	-7.3	-2.6	-8.4	-8.2
3.30	-15.2	-9.4	-6.9	-2.3	-7.9	-7.8
3.40	-14.0	-8.8	-6.6	-2.1	-7.5	-7.4
3.60	-11.8	-7.8	-5.9	-1.7	-6.8	-6.7
3.80	-10.1	-6.9	-5.3	-1.5	-6.1	-6.0

4.00	-8.6	-6.1	-4.8	-1.2	-5.5	-5.4
4.50	-5.8	-4.6	-3.8	-0.8	-4.3	-4.2
5.00	-3.9	-3.5	-3.0	-0.6	-3.4	-3.3

Table 3S Interaction energy (kcal/mol) of NH_4^+ and benzene complex calculated at MP2/aug-cc-pVTZ, PM3/MMpol and PM3/MM levels of theory

R (Å)	MP2	QM/MMpol			QM/MM	
	E_{inter}	E_{inter}	$E^{el,q'}_{QM/MMpol}$	$E^{el,\boldsymbol{\mu}}_{QM/MMpol}$	E_{inter}	$E^{el,q}_{QM/MM}$
2.40	-7.1	-2.9	-15.8	-6.8	1.6	-18.0
2.50	-12.9	-9.2	-14.8	-5.9	-5.3	-16.8
2.60	-16.7	-12.6	-13.8	-5.2	-9.2	-15.7
2.70	-18.9	-14.2	-12.9	-4.7	-11.3	-14.7
2.80	-20.1	-14.8	-12.1	-4.2	-12.3	-13.7
2.90	-20.4	-14.7	-11.3	-3.7	-12.5	-12.8
3.00	-20.3	-14.3	-10.6	-3.3	-12.4	-12.0
3.10	-19.7	-13.7	-9.9	-3.0	-12.0	-11.2
3.20	-18.9	-13.0	-9.3	-2.7	-11.5	-10.5
3.30	-18.0	-12.2	-8.7	-2.5	-10.9	-9.9
3.40	-17.0	-11.5	-8.2	-2.2	-10.3	-9.3
3.50	-15.9	-10.8	-7.7	-2.0	-9.7	-8.7
3.60	-14.9	-10.1	-7.2	-1.9	-9.2	-8.2
3.70	-13.9	-9.4	-6.8	-1.7	-8.6	-7.7
3.80	-13.0	-8.8	-6.4	-1.6	-8.1	-7.2
3.90	-12.1	-8.2	-6.0	-1.4	-7.6	-6.8
4.00	-11.3	-7.7	-5.7	-1.3	-7.1	-6.4
4.10	-10.5	-7.2	-5.4	-1.2	-6.7	-6.1
4.20	-9.8	-6.7	-5.1	-1.1	-6.3	-5.7
4.30	-9.1	-6.3	-4.8	-1.0	-5.9	-5.4
4.40	-8.5	-5.9	-4.5	-0.9	-5.6	-5.1
4.50	-8.0	-5.6	-4.3	-0.9	-5.3	-4.9
4.60	-7.5	-5.3	-4.1	-0.8	-5.0	-4.6

4.70	-7.0	-4.9	-3.9	-0.8	-4.7	-4.4
5.00	-5.8	-4.2	-3.3	-0.6	-4.0	-3.8
5.50	-4.3	-3.2	-2.6	-0.4	-3.1	-3.0
6.00	-3.3	-2.5	-2.1	-0.3	-2.5	-2.4

Table 4S Interaction energy (kcal/mol) of the S22 set. The reference energy is at CCSD(T) complete basis set level of theory[26]

		QM region	Ref[26]	PM3/MMpol	PM3/MM
Hydrogen bonded complexes (7)					
1	Ammonia dimer (C_{2h})	*Ammonia*	-3.2	-2.0	-2.2
2	Water dimer (C_s)	*Donor*	-5.0	-3.2	-3.5
		Acceptor	-5.0	-3.6	-3.9
3	Formic acid dimer (C_{2h})	*Formic acid*	-18.6	-12.7	-10.1
4	Formamide dimer (C_{2h})	*Formamide*	-16.0	-8.9	-8.5
5	Uracil dimer (C_{2h})	*Uracil*	-20.7	-12.7	-13.6
6	2-pyridoxine 2-aminopyridine (C_1)	*2-py*	-16.7	-8.0	-9.6
		2-am	-16.7	-9.9	-9.8
7	Adenine thymine WC (C_1)	*Adenine*	-16.4	-10.0	-10.1
		Thymine	-16.4	-8.3	-9.2
MUE				**5.5**	**5.4**
MSE				**5.5**	**5.4**
Complexes with predominant dispersion contribution (8)					
8	Methane dimer (D_{3d})	*Methane*	-0.5	-0.5	-0.5
9	Ethene dimer (D_{2d})	*Ethene*	-1.5	-0.8	-0.8
10	Benzene methane (C_3)	*Benzene*	-1.5	-1.0	-1.0
		Methane	-1.5	-1.0	-1.1
11	Benzene dimer (C_{2h})	*Benzene*	-2.7	-2.7	-2.6
12	Pyrazine dimer (C_s)	*Pyrazine*	-4.4	-5.1	-5.3
13	Uracil dimer (C_2)	*Uracil*	-10.1	-8.9	-9.3
14	Indole benzene (C_1)	*Indole*	-5.2	-5.4	-5.6
		Benzene	-5.2	-4.1	-4.0
15	Adenine thymine stack (C_1)	*Adenine*	-12.2	-11.6	-12.2

		Thymine	-12.2	-11.7	-12.9
MUE				**0.6**	**0.5**
MSE				**0.4**	**0.2**
Mixed complexes (7)					
16	Ethene ethyne (C_{2v})	*Ethene*	-1.5	-0.7	-0.6
		Ethyne	-1.5	-0.9	-0.7
17	Benzene water (C_s)	*Benzene*	-3.3	-2.0	-2.2
		Water	-3.3	-3.3	-3.4
18	Benzene ammonia (C_s)	*Benzene*	-2.4	-1.5	-1.6
		Ammonia	-2.4	-2.7	-2.9
19	Benzene HCN (C_s)	*Benzene*	-4.5	-2.6	-2.5
		HCN	-4.5	-3.0	-3.2
20	Benzene dimer (C_{2v})	*Vertical*	-2.7	-1.9	-2.0
		Horizontal	-2.7	-1.8	-1.8
21	Indole benzene T-shape (C_1)	*Indole*	-5.7	-5.4	-5.6
		Benzene	-5.7	-4.1	-4.1
22	Phenol dimer (C_1)	*Donor*	-7.1	-4.2	-5.1
		Acceptor	-7.1	-4.7	-5.3
MUE				**1.2**	**1.1**
MSE				**1.1**	**1.0**
Overall					
MUE				**2.2**	**2.1**
MSE				**2.2**	**2.0**
r^2				**0.9**	**0.9**

Table 5S Electrostatic energy contribution (kcal/mol) of the point charges and/or dipoles in the MM region to the total interaction energy of the S22 set.

		QM region	PM3/MMpol		PM3/MM
Hydrogen bonded complexes (7)			Charge	Dipole	Charge
1	Ammonia dimer (C_{2h})	*Ammonia*	-1.86	-0.13	-2.11
2	Water dimer (C_s)	*Donor*	-3.35	-0.11	-3.85
		Acceptor	-3.68	-0.17	-4.20
3	Formic acid dimer (C_{2h})	*Formic acid*	-13.21	-0.50	-10.43
4	Formamide dimer (C_{2h})	*Formamide*	-8.15	-0.34	-8.00
5	Uracil dimer (C_{2h})	*Uracil*	-11.60	-0.56	-13.01
6	2-pyridoxine 2-aminopyridine (C_1)	*2-py*	-6.41	-0.40	-8.52
		2-am	-8.48	-0.36	-8.69
7	Adenine thymine WC (C_1)	*Adenine*	-8.20	-0.45	-8.67
		Thymine	-6.52	-0.18	-7.72
Complexes with predominant dispersion contribution (8)					
8	Methane dimer (D_{3d})	*Methane*	0.03	0.00	0.01
9	Ethene dimer (D_{2d})	*Ethene*	-0.11	0.00	-0.07
10	Benzene methane (C_3)	*Benzene*	-0.03	-0.01	-0.01
		Methane	-0.07	0.00	-0.09
11	Benzene dimer (C_{2h})	*Benzene*	0.71	-0.02	0.69
12	Pyrazine dimer (C_s)	*Pyrazine*	-1.13	-0.01	-1.43
13	Uracil dimer (C_2)	*Uracil*	-2.97	-0.17	-3.66
14	Indole benzene (C_1)	*Indole*	-2.20	-0.14	-2.59
		Benzene	0.22	-0.01	-0.25
15	Adenine thymine stack (C_1)	*Adenine*	-4.05	-0.07	-4.72
		Thymine	-3.74	-0.20	-5.31

Mixed complexes (7)					
16	Ethene ethyne (C_{2v})	*Ethene*	-0.10	-0.26	0.00
		Ethyne	-0.35	-0.56	-0.01
17	Benzene water (C_s)	*Benzene*	-1.26	-1.10	-0.02
		Water	-2.76	-2.43	-0.12
18	Benzene ammonia (C_s)	*Benzene*	-0.54	-0.46	-0.02
		Ammonia	-1.94	-1.71	-0.06
19	Benzene HCN (C_s)	*Benzene*	-1.28	-1.32	-0.01
		HCN	-2.40	-2.09	-0.11
20	Benzene dimer (C_{2v})	*Vertical*	-0.51	-0.44	-0.01
		Horizontal	-0.29	-0.25	-0.01
21	Indole benzene T-shape (C_1)	*Indole*	-2.99	-2.61	-0.19
		Benzene	-1.32	-1.31	-0.02
22	Phenol dimer (C_1)	*Donor*	-3.08	-2.13	-0.13
		Acceptor	-3.62	-2.82	-0.09