Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Estimation procedure of the MP2 and CCSD(T) level interaction energies for the halogen-bonded clusters at the basis set limit.

Estimation procedure of MP2 level interaction energy at the basis set limit

The MP2 level interaction energy at the basis set limit [$E_{MP2(limit)}$] for the halogen-bonded cluster was obtained by Helgaker et al.'s method from the MP2 interaction energies (E_{MP2}) obtained using the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets. In Helgaker et al.'s method the calculated E_{MP2} were fitted to a form a + b X^{-3} (where X is 2 for aug-cc-pVDZ, 3 for aug-cc-pVTZ and 4 for aug-cc-pVQZ). The $E_{MP2(limit)}$ was then calculated by an extrapolation. Helgaker et al.'s method was originally proposed for calculating the electron correlation contribution at the basis set limit. But we used this method to calculated the $E_{MP2(limit)}$, since the basis set dependence of HF level interaction energy (E_{HF}) is small. The E_{MP2} calculated for the halogen bonded-clusters using the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets and the $E_{MP2(limit)}$ obtained by Helgaker et al.'s method are summarized in Tables 1S and 2S.

Estimation procedure of CCSD(T) level interaction energy at the basis set limit

The CCSD(T) level interaction energy at the basis set limit [$E_{CCSD(T)(limit)}$] for the halogen-bonded cluster was obtained according to equation (1)

$$E_{CCSD(T)(limit)} = E_{MP2(limit)} + \Delta CCSD(T)(limit), \quad (1)$$

where ΔCCSD(T)(limit) denotes the CCSD(T) correction term [ΔCCSD(T)] at the basis set limit. The ΔCCSD(T) [= $E_{CCSD(T)}$ - E_{MP2}] is the difference between the CCSD(T) level interaction energy [$E_{CCSD(T)}$] and the MP2 level interaction energy (E_{MP2}). The ΔCCSD(T)(limit) was obtained by equation (2)

$$\Delta CCSD(T)(limit) = \Delta CCSD(T)(M) + \Delta(M)\Delta CCSD(T), \quad (2)$$

where ΔCCSD(T)(M) denotes ΔCCSD(T) obtained using a Medium size basis set. The cc-pVDZ basis set was used for the Medium size basis set in this work. The ΔCCSD(T) has a weak basis set dependence. Δ(M)ΔCCSD(T) is a correction term for slight underestimation of the ΔCCSD(T) by the Medium size basis set. The Δ(M)ΔCCSD(T) corresponds to a difference between the ΔCCSD(T)(limit) and ΔCCSD(T)(M).

We can calculate the Δ(M)ΔCCSD(T), if we know the value of $F_{corr(M)}$, which is defined by equation (3)

$$F_{corr(M)} = \Delta CCSD(T)(M)/\Delta CCSD(T)(limit) \quad (3).$$

From equations (2) and (3) we can obtained equation (4)

$$\Delta(M)\Delta CCSD(T) = \Delta CCSD(T)(M) \times (1 - F_{corr(M)})/F_{corr(M)} \quad (4).$$

We calculated the $F_{corr(M)}$ value by equation (5) in this work

$$F_{corr(M)} = E_{corr(MP2)(M)}/E_{corr(MP2)(limit)} \quad (5),$$

where the $E_{corr(MP2)(M)}$ denotes the MP2 level electron correlation effect on the calculated interaction energy ($E_{corr(MP2)} = E_{MP2} - E_{HF}$) using the medium size basis set. The $E_{corr(MP2)(limit)}$ denotes the MP2 level electron correlation effect at the basis set limit (= $E_{MP2(limit)} - E_{HF(limit)}$). We can obtain sufficiently accurate $F_{corr(M)}$ value by equation (5), if

the basis set dependence of the CCSD(T) level electron correlation effect is close to that of $E_{corr(MP2)}$. The E_{HF} calculated using the cc-pVQZ basis set was used as the $E_{HF(limit)}$, since the basis set dependence of the E_{HF} is very small. The energy terms used for calculating the $E_{CCSD(T)(limit)}$ are summarized in Table 3S.

TABLE 1S. HF and MP2 Interaction Energies Calculated for Halogen-Bonded Clusters[a]

complex	E_{HF}[b]			E_{MP2}[b]		
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
1	-0.421	-0.255	-0.235	-3.753	-4.072	-4.252
2	-0.821	-0.644	-0.625	-4.282	-4.614	-4.812
3	-0.803	-0.613	-0.595	-4.263	-4.600	-4.807
4	-0.756	-0.568	-0.549	-4.228	-4.563	-4.770
5	-0.648	-0.468	-0.451	-4.101	-4.440	-4.640
6	-1.058	-0.881	-0.863	-4.521	-4.876	-5.083
7	-1.580	-1.400	-1.381	-4.898	-5.266	-5.479
8	-1.375	-1.201	-1.184	-4.822	-5.194	-5.404
9	-0.294	-0.124	-0.106	-3.704	-4.032	-4.219
10	-0.239	-0.075	-0.058	-3.623	-3.941	-4.124
11	-0.205	-0.040	-0.021	-3.586	-3.909	-4.093
12	-0.804	-0.625	-0.604	-4.378	-4.709	-4.910
13	-0.832	-0.638	-0.608	-4.356	-4.695	-4.868
14	-0.821	-0.628	-0.608	-4.329	-4.662	-4.869
15	-0.849	-0.669	-0.650	-4.229	-4.567	-4.765
16	-0.972	-0.797	-0.778	-4.567	-4.925	-5.130
17	-1.375	-1.196	-1.180	-4.998	-5.369	-5.584
18	-1.259	-1.084	-1.068	-4.923	-5.295	-5.510
19	-0.597	-0.425	-0.405	-3.833	-4.156	-4.341
20	-0.305	-0.143	-0.124	-3.601	-3.919	-4.099
21	-0.438	-0.272	-0.253	-3.664	-3.984	-4.166
22	-0.859	-0.682	-0.662	-4.582	-4.923	-5.136
23	-0.885	-0.684	-0.661	-4.542	-4.892	-5.105
24	-0.849	-0.649	-0.627	-4.494	-4.834	-5.047
25	-0.889	-0.695	-0.677	-4.494	-4.835	-5.040
26	-1.374	-1.154	-1.140	-5.246	-5.606	-5.840
27	-1.317	-1.123	-1.105	-4.726	-5.082	-5.295
28	-1.662	-1.429	-1.415	-5.604	-5.981	-6.232
29	-1.580	-1.374	-1.356	-5.036	-5.409	-5.637
30	-2.670	-2.404	-2.392	-6.672	-7.094	-7.381
31	-1.634	-1.435	-1.417	-5.056	-5.409	-5.631
32	-1.642	-1.430	-1.412	-5.068	-5.433	-5.662
33	-1.624	-1.413	-1.394	-5.068	-5.433	-5.663

[a] Energies in kcal mol^{-1}.

[b] BSSE corrected interaction energies.

TABLE 2S. MP2 Level Interaction Energies at the Basis Set Limit Calculated for Halogen-Bonded Clusters[a]

comoplex	$E_{MP2(limit)}$[b]		
	DT[c]	TQ[d]	DTQ[e]
1	-4.207	-4.384	-4.280
2	-4.754	-4.956	-4.838
3	-4.742	-4.958	-4.832
4	-4.705	-4.921	-4.795
5	-4.583	-4.786	-4.667
6	-5.025	-5.235	-5.112
7	-5.421	-5.634	-5.510
8	-5.350	-5.557	-5.436
9	-4.170	-4.356	-4.247
10	-4.075	-4.258	-4.151
11	-4.046	-4.227	-4.121
12	-4.849	-5.057	-4.935
13	-4.838	-4.993	-4.902
14	-4.803	-5.020	-4.893
15	-4.710	-4.910	-4.793
16	-5.075	-5.279	-5.160
17	-5.525	-5.741	-5.615
18	-5.452	-5.666	-5.541
19	-4.293	-4.475	-4.368
20	-4.053	-4.231	-4.127
21	-4.119	-4.299	-4.193
22	-5.067	-5.291	-5.160
23	-5.039	-5.260	-5.131
24	-4.977	-5.202	-5.070
25	-4.978	-5.189	-5.066
26	-5.757	-6.011	-5.863
27	-5.232	-5.450	-5.322
28	-6.139	-6.415	-6.254
29	-5.567	-5.803	-5.665
30	-7.271	-7.590	-7.404
31	-5.558	-5.792	-5.655
32	-5.587	-5.829	-5.687
33	-5.587	-5.831	-5.688

[a] Energies in kcal mol^{-1}.

[b] MP2 interaction energies at the basis set limit obtained by Helgaker et al.'s method.

[c] Estimated from the interaction energies calculated using the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

[c] Estimated from the interaction energies calculated using the aug-cc-pVTZ and aug-cc-pVQZ basis sets.

[c] Estimated from the interaction energies calculated using the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets.

TABLE 3S. Some Energy Terms Used for Calculating CCSD(T) Interaction Energies at the Basis Set Limit for Halogen-Bonded Clusters[a]

	$E_{HF(limit)}$[b]	$E_{MP2(limit)}$[c]	$E_{corr(MP2)(limit)}$[d]	$E_{HF(M)}$[e]	$E_{MP2(M)}$[e]	$E_{CCSD(T)(M)}$[e]
1	-0.235	-4.280	-4.045	-0.661	-3.058	-2.489
2	-0.625	-4.838	-4.212	-1.148	-3.643	-3.022
3	-0.595	-4.832	-4.237	-1.082	-3.543	-2.922
4	-0.549	-4.795	-4.245	-1.052	-3.514	-2.891
5	-0.451	-4.667	-4.216	-0.942	-3.381	-2.765
6	-0.863	-5.112	-4.249	-1.376	-3.770	-3.155
7	-1.381	-5.510	-4.129	-1.915	-4.093	-3.517
8	-1.184	-5.436	-4.252	-1.651	-4.058	-3.444
9	-0.106	-4.247	-4.141	-0.538	-2.964	-2.366
10	-0.058	-4.151	-4.094	-0.497	-2.946	-2.373
11	-0.021	-4.121	-4.100	-0.464	-2.881	-2.301
12	-0.604	-4.935	-4.331	-1.127	-3.722	-3.063
13	-0.608	-4.902	-4.294	-1.109	-3.619	-2.976
14	-0.608	-4.893	-4.285	-1.116	-3.597	-2.962
15	-0.650	-4.793	-4.143	-1.142	-3.485	-2.895
16	-0.778	-5.160	-4.382	-1.287	-3.805	-3.131
17	-1.180	-5.615	-4.435	-1.719	-4.191	-3.471
18	-1.068	-5.541	-4.473	-1.537	-4.145	-3.435
19	-0.405	-4.368	-3.963	-0.843	-3.073	-2.554
20	-0.124	-4.127	-4.003	-0.556	-2.915	-2.383
21	-0.253	-4.193	-3.941	-0.693	-2.935	-2.428
22	-0.662	-5.160	-4.499	-1.183	-3.882	-3.213
23	-0.661	-5.131	-4.470	-1.157	-3.735	-3.076
24	-0.627	-5.070	-4.443	-1.155	-3.713	-3.054
25	-0.677	-5.066	-4.389	-1.171	-3.705	-3.038
26	-1.140	-5.863	-4.723	-1.700	-4.373	-3.604
27	-1.105	-5.322	-4.217	-1.663	-3.934	-3.326
28	-1.415	-6.254	-4.839	-2.045	-4.708	-3.907
29	-1.356	-5.665	-4.308	-1.962	-4.212	-3.569
30	-2.392	-7.404	-5.012	-3.138	-5.645	-4.776
31	-1.417	-5.655	-4.239	-2.049	-4.344	-3.719
32	-1.412	-5.687	-4.276	-2.013	-4.270	-3.641
33	-1.394	-5.688	-4.294	-2.010	-4.267	-3.632

	$\Delta CCSD(T)(M)$[f]	$E_{corr(MP2)(M)}$[g]	$\Delta(M)E_{corr(MP2)}$[h]	$\Delta(M)DCCSD(T)$[i]	$\Delta CCSD(T)_{(limit)}$[j]	$E_{CCSD(T)(limit)}$[k]
1	0.569	-2.397	-1.648	0.392	0.961	-3.320
2	0.621	-2.495	-1.717	0.427	1.048	-3.789
3	0.620	-2.460	-1.777	0.448	1.068	-3.764
4	0.622	-2.461	-1.784	0.451	1.073	-3.721
5	0.616	-2.439	-1.777	0.448	1.064	-3.603
6	0.615	-2.394	-1.855	0.476	1.091	-4.021
7	0.576	-2.178	-1.951	0.516	1.092	-4.417
8	0.614	-2.407	-1.845	0.471	1.085	-4.351
9	0.598	-2.426	-1.715	0.423	1.021	-3.226
10	0.573	-2.448	-1.646	0.385	0.958	-3.194
11	0.581	-2.417	-1.683	0.404	0.985	-3.136
12	0.659	-2.596	-1.735	0.441	1.100	-3.835
13	0.643	-2.510	-1.784	0.457	1.100	-3.802
14	0.635	-2.482	-1.803	0.462	1.097	-3.796

15	0.589	-2.343	-1.800	0.453	1.042	-3.751
16	0.674	-2.518	-1.864	0.499	1.173	-3.986
17	0.720	-2.472	-1.963	0.572	1.292	-4.323
18	0.711	-2.609	-1.864	0.507	1.218	-4.322
19	0.519	-2.229	-1.734	0.404	0.923	-3.446
20	0.532	-2.359	-1.644	0.371	0.903	-3.224
21	0.507	-2.242	-1.699	0.384	0.891	-3.302
22	0.669	-2.699	-1.800	0.446	1.115	-4.045
23	0.660	-2.578	-1.892	0.484	1.144	-3.987
24	0.659	-2.559	-1.884	0.486	1.145	-3.926
25	0.667	-2.533	-1.856	0.488	1.155	-3.911
26	0.769	-2.673	-2.050	0.589	1.358	-4.504
27	0.608	-2.272	-1.945	0.521	1.129	-4.193
28	0.802	-2.663	-2.176	0.654	1.456	-4.798
29	0.644	-2.250	-2.058	0.588	1.232	-4.433
30	0.868	-2.507	-2.505	0.868	1.736	-5.668
31	0.625	-2.295	-1.944	0.528	1.153	-4.502
32	0.629	-2.257	-2.019	0.563	1.192	-4.496
33	0.635	-2.258	-1.916	0.540	1.208	-4.480

[a] Energies in kcal mol^{-1}.

[b] HF interaction energies at the basis set limit. HF/aug-cc-pVQZ interaction energies were used. See text.

[c] MP2 interaction energies at the basis set limit estimated from the MP2 interaction energies calculated using the aug-cc-pVXZ (X = D, T and Q) basis sets by Helgaker et al.'s method. See text.

[d] MP2 correlation interaction energies at the basis set limit [= $E_{MP2(limit)} - E_{HF(limit)}$]. See text.

[e] HF, MP2 and CCSD(T) interaction energies calculated using the Medium size basis sets (cc-pVDZ basis set). See text.

[f] CCSD(T) correction terms calculated using the Medium size basis set [= $E_{CCSD(T)(M)} - E_{MP2(M)}$]. See text.

[g] MP2 correlation interaction energies calculated using the Medium size basis set [= $E_{MP2(M)} - E_{HF(M)}$]. See text.

[h] Underestimation of MP2 correlation interaction energies by the Medium size basis set [= $E_{corr(MP2)(limit)} - E_{corr(MP2)(M)}$]. See text.

[i] Underestimation of CCSD(T) correction terms by the Medium size basis set. See text.

[j] Calculated CCSD(T) correction terms at the basis set limit [= ΔCCSD(T)(M) + Δ(M)ΔCCSD(T)]. See text.

[k] Calculated CCSD(T) interaction energies at the basis set limit [= $E_{MP2(limit)}$ + ΔCCSD(T)(limit)]. See text.

TABLE 4S. MP2 Interaction Energies and Interaction Energies at the Basis set Limit Calculated for Pyridine Clusters with Bromobenzene and Chlorobenzene[a]

complex	E_{MP2}[b]			$E_{MP2(limit)}$[c]
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	
C6H5Cl-C5H5N				
Dunning[d]	-1.307	-1.436	-1.485	-1.503
DGDZVP[e]	-1.160	-1.371	-1.478	-1.500
C6H5Br-C5H5N				
Dunning[d]	-2.476	-2.644	-2.721	-2.741
DGDZVP[e]	-2.325	-2.557	-2.688	-2.709
aug-cc-pVXZ-PP[f]	-2.671	-2.821	-2.902	-2.916
C6H5I-C5H5N				
DGDZVP[e]	-3.753	-4.072	-4.252	-4.280
aug-cc-pVXZ-PP[f]	-4.275	-4.535	-4.661	-4.689
para-FC6H4I-C5H5N				
DGDZVP[e]	-4.101	-4.440	-4.640	-4.667
aug-cc-pVXZ-PP[f]	-4.644	-4.940	-5.077	-5.111

[a] Energies in kcal mol^{-1}.

[b] BSSE corrected interaction energies.

[c] MP2 interaction energies at the basis set limit estimated by Helgaker et al.'s method. See text.

[d] Dunning's aug-cc-pVXZ basis set was used for all atoms.

[e] DGDZVP basis set was used for halogen atoms. Dunning's aug-cc-pVXZ basis set was used for other atoms.

[f] aug-cc-pVXZ-PP basis set was used for halogen atoms. Dunning's aug-cc-pVXZ basis set was used for other atoms.