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The Influence of Large-Amplitude Librational Motion on the Hydrogen Bond Energy of Alcohol-Water Complexes

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Supporting Information

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Table 1: The predicted absolute electronic energy E_{abs} (Hartrees) and dissociation energies D_e (kJ/mol) for mixed water/methanol (wm, most stable) and methanol/water (mw, less stable) complexes at the B3LYP, B3LYP-D3 and CCSD(T) levels based on fully geometry optimized monomers at the B3LYP and B3LYP-D3 levels employing the aug-cc-pVTZ basis set (aTZ) together with the difference of electronic dissociation energy between the two different conformers ΔE_e (kJ/mol).

	B3LYP/aTZ (geo)[a] B3LYP/aTZ (el)		B3LYP-CP/aTZ (geo)[a,b] B3LYP/aTZ (el)		B3LYP-CP/aTZ (geo)[a,b] CCSD(T)/aTZ (el)	
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e
w	–76.4661966				–76.3423052	
m	–115.7767608				–115.5623521	
mw	–192.2499676	18.40	–192.2498672	18.14	–191.9130798	22.11
wm	–192.2507980	20.58	–192.2506884	20.29	–191.9140428	24.64
ΔE_e		2.18		2.16		2.53
	B3LYP-D3/aTZ (geo)[a] B3LYP-D3/aTZ (el)		B3LYP-D3-CP/aTZ (geo)[a,b] B3LYP-D3/aTZ (el)		B3LYP-D3-CP/aTZ (geo)[a,b] CCSD(T)/aTZ (el)	
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e
w	–76.4662050				–76.3423045	
m	–115.7778700				–115.5623487	
mw	–192.2525084	22.14	–192.2524015	21.86	–191.9131025	22.18
wm	–192.2536639	25.18	–192.2535506	24.88	–191.9141454	24.92
ΔE_e		3.03		3.02		2.74

[a] RMS force criterion set to 10^{-6} (atomic units) for all geometry optimizations.

[b] CP = Counterpoise Correction applied.

Table 2: The predicted absolute electronic energy E_{abs} (Hartrees) and dissociation energies D_e (kJ/mol) for mixed water/methanol (wm, most stable) and methanol/water (mw, less stable) complexes at the MP2, CCSD(T) and CCSD(T)-F12 levels based on fully geometry optimized monomers at the MP2 level employing the aug-cc-pVTZ (aTZ) and aug-cc-pVQZ (aQZ) basis sets together with the difference of electronic dissociation energy between the two different conformers ΔE_e (kJ/mol).

	MP2/aTZ (geo)[a] MP2/aTZ (el)		MP2-CP/aTZ (geo)[a,b] MP2/aTZ (el)		MP2-CP/aTZ (geo)[a,b] CCSD(T)/aTZ (el)		MP2-CP/aTZ (geo)[a,b] CCSD(T)-F12/aTZ (el)			
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e		
w	–76.3289923				–76.3423045		–76.4094478			
m	–115.5290078				–115.5623571		–115.6872606			
mw	–191.8663630	21.96	–191.8655547	19.83	–191.9131145	22.19	–192.1050794	21.98		
wm	–191.8675446	25.06	–191.8666499	22.71	–191.9141887	25.01	–192.1060874	24.62		
ΔE_e		3.10		2.88		2.82		2.65		
	MP2/aQZ (geo)[a] MP2/aQZ (el		MP2-CP/aQZ (geo)[a,b] MP2/aQZ (el)		MP2-CP/aQZ (geo)[a,b] CCSD(T)/aTZ (el)		MP2-CP/aQZ (geo)[a,b] CCSD(T)-F12/aTZ (el)		MP2-CP/aQZ (geo)[a,b] CCSD(T)-F12/aQZ (el)	
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e
w	–76.3519184				–76.3423119		–76.40946628		–76.42224865	
m	–115.5631124				–115.5623083		–115.68728478		–115.7054932	
mw	–191.9232089	21.47	–191.9228192	20.45	–191.9130617	21.95	–192.10513507	22.01	–192.1359375	21.51
wm	–191.9243758	24.54	–191.9239285	23.36	–191.9141373	24.74	–192.10614383	24.66	–192.1369574	24.20
ΔE_e		3.06		2.91		2.82		2.65		2.68

[a] RMS force criterion set to 10^{-6} (atomic units) for all geometry optimizations.

[b] CP = Counterpoise Correction applied.

Table 3: The predicted absolute electronic energy E_{abs} (Hartrees) and dissociation energies D_e (kJ/mol) for mixed water/t-butyl alcohol (wt, most stable) and t-butyl alcohol/water (tw, less stable) complexes at the B3LYP, B3LYP-D3 and CCSD(T) levels based on fully geometry optimized monomers at the B3LYP and B3LYP-D3 levels employing the aug-cc-pVTZ basis set (aTZ) together with the difference of electronic dissociation energy between the two different conformers ΔE_e (kJ/mol).

	B3LYP/aTZ (geo)[a] B3LYP/aTZ (el)		B3LYP-CP/aTZ (geo)[a,b] B3LYP/aTZ (el)		B3LYP-CP/aTZ (geo)[a,b] CCSD(T)/aTZ (el)	
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e
w	–76.4661966				–76.3423052	
t	–233.7744275				–233.3066355	
tw	–310.2468571	16.36	–310.2467263	16.02	–309.6576423	22.85
wt	–310.2489775	21.93	–310.2488297	21.54	–309.6599097	28.80
ΔE_e		5.57		5.52		5.95
	B3LYP-D3/aTZ (geo)[a] B3LYP-D3/aTZ (el)		B3LYP-D3-CP/aTZ (geo)[a,b] B3LYP-D3/aTZ (el)		B3LYP-D3-CP/aTZ (geo)[a,b] CCSD(T)/aTZ (el)	
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e
w	–76.4662050				–76.3423045	
t	–233.7849828				–233.3066616	
tw	–310.2596343	22.18	–310.2594915	21.80	–309.6578720	23.38
wt	–310.2628379	30.59	–310.2626699	30.15	–309.6604021	30.03
ΔE_e		8.41		8.34		6.64

[a] RMS force criterion set to 10^{-6} (atomic units) for all geometry optimizations.

[b] CP = Counterpoise Correction applied.

Table 4: The predicted absolute electronic energy E_{abs} (Hartrees) and dissociation energies D_e (kJ/mol) for mixed water/*t*-butyl alcohol (wt, most stable) and *t*-butyl alcohol/water (tw, less stable) complexes at the MP2, CCSD(T) and CCSD(T)-F12 levels based on fully geometry optimized monomers at the MP2 level employing the aug-cc-pVTZ (aTZ) basis set together with the difference of electronic dissociation energy between the two different conformers ΔE_e (kJ/mol).

	MP2/aTZ (geo)[a] MP2/aTZ (el)		MP2-CP/aTZ (geo)[a,b] MP2/aTZ (el)		MP2-CP/aTZ (geo)[a,b] CCSD(T)/aTZ (el)		MP2/aTZ (geo)[a,b] CCSD(T)-F12/aTZ (el)	
	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e	E_{abs}	D_e
w	–76.3289923				–76.3423045		–76.4094478	
t	–233.2210850				–233.3066372		–233.6062126	
tw	–309.5589091	23.19	–309.5578621	20.44	–309.6578587	23.41	–310.0243343	22.77
wt	–309.5615378	30.09	–309.5602656	26.75	–309.6603926	30.06	–310.0268163	29.29
ΔE_e		6.90		6.31		6.65		6.52

[a] RMS force criterion set to 10^{-6} (atomic units) for all geometry optimizations.

[b] CP = Counterpoise Correction applied.

Table 5: The predicted harmonic vibrational zero-point energies (ZPE) for mixed isotopic complexes of water (w) with methanol (m) and *t*-butyl alcohol (t) at the MP2/aug-cc-pVTZ level.

	H_2O–CH_3OH	CH_3OH–H_2O	H_2O–CD_3OD	CD_3OD–H_2O	D_2O–CH_3OH	CH_3OH–D_2O
ZPE_m	136.18		101.83		136.18	
ZPE_w	56.21		56.21		40.89	
ZPE	200.19	198.98	165.56	163.94	183.32	182.92
ΔZPE	7.80	6.59	7.52	5.90	6.25	5.85
	H_2O–$C(CH_3)_3OH$	$C(CH_3)_3OH$–H_2O	H_2O–$C(CD_3)_3OD$	$C(CD_3)_3OD$–H_2O	D_2O–$C(CH_3)_3OH$	$C(CH_3)_3OH$–D_2O
ZPE_t	358.61		273.10		358.61	
ZPE_w	56.21		56.21		40.89	
ZPE	423.22	421.16	337.02	334.75	405.93	404.81
ΔZPE	8.40	6.34	8.06	5.74	6.77	5.57