Supporting Information

Compensation Relationship in Thermodynamics of Gas-Phase Molecular Complexation

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Table S1

The electronic binding energies (*BE*), changes in zero-point vibrational energies (Δ*ZPVE*) and thermal corrections ($\Delta E_{\mathrm{vib,therm}}$), and binding enthalpy of gas-phase molecular complexation computed in this work. All values are given in kJ·mol^{-1}.

Compound A	Compound B	*BE*	Δ*ZPVE*	$\Delta E_{\mathrm{vib,therm}}$	$\Delta_{\mathrm{bind}}H$
water	water	–21.13	8.78	8.17	–14.09
water	dimethyl ether	–24.67	7.76	9.31	–17.50
hydrogen fluoride	hydrogen fluoride	–19.16	7.44	4.24	–14.92
hydrogen fluoride	water	–36.32	11.15	4.47	–29.37
hydrogen fluoride	dimethyl ether	–42.81	9.76	6.06	–35.66
hydrogen fluoride	methyl ethyl ether	–45.21	9.55	5.93	–38.41
hydrogen fluoride	diethyl ether	–46.40	10.15	5.85	–39.08
hydrogen chloride	dimethyl ether	–29.09	7.13	6.90	–23.74
methanol	methanol	–24.01	5.80	10.98	–17.15
methanol	methylamine	–31.45	6.45	10.42	–24.49
methanol	dimethylamine	–33.24	5.87	10.89	–26.40
methanol	trimethylamine	–34.33	4.93	9.07	–30.25
methanol	triethylamine	–36.69	6.65	10.68	–29.27
ethanol	ethanol	–27.46	6.12	10.85	–20.40
1-propanol	1-propanol	–30.97	5.74	10.94	–24.20
2-propanol	2-propanol	–29.58	5.30	11.59	–22.60
2-butanol	2-butanol	–29.03	4.45	9.55	–24.95
tert-butyl alcohol	*tert*-butyl alcohol	–31.63	5.13	9.28	–27.13
trifluoroethanol	methanol	–34.11	5.56	8.55	–29.91
trifluoroethanol	trifluoroethanol	–31.12	4.63	11.69	–24.72
trifluoroethanol	propanal	–37.04	5.13	11.44	–30.39
trifluoroethanol	diethyl ether	–35.57	5.44	11.63	–28.41
trifluoroethanol	acetone	–39.69	5.23	11.14	–33.24
trifluoroethanol	tetrahydrofuran	–40.41	5.26	9.34	–35.73
trifluoroethanol	ammonia	–38.42	7.52	9.28	–31.55
trifluoroethanol	pyridine	–43.58	4.26	11.88	–37.35
trifluoroethanol	trimethylamine	–48.57	5.24	11.26	–41.98
trifluoroethanol	triethylamine	–51.35	6.34	10.84	–44.09
trifluoroethanol	tetramethylguanidine	–55.30	4.60	8.90	–51.71
hexafluoro-2-propanol	methanol	–39.58	5.62	10.72	–33.16
hexafluoro-2-propanol	diethyl ether	–41.79	5.00	11.63	–35.08
hexafluoro-2-propanol	acetone	–40.89	4.80	11.13	–34.88
hexafluoro-2-propanol	tetrahydrofuran	–44.20	4.46	9.28	–40.38
hexafluoro-2-propanol	ammonia	–45.59	7.32	9.03	–39.15
hexafluoro-2-propanol	trimethylamine	–58.56	4.65	8.73	–55.10
hexafluoro-2-propanol	triethylamine	–59.85	4.87	10.76	–54.14
perfluoro-*tert*-butanol	diethyl ether	–48.06	5.17	8.86	–43.95
perfluoro-*tert*-butanol	acetone	–46.72	4.52	11.11	–41.00
perfluoro-*tert*-butanol	tetrahydrofuran	–52.75	4.16	6.76	–51.74
perfluoro-*tert*-butanol	ammonia	–52.83	7.29	8.84	–46.61
perfluoro-*tert*-butanol	trimethylamine	–68.27	4.15	11.04	–63.00

Compound A	Compound B	*BE*	Δ*ZPVE*	$\Delta E_{\mathrm{vib,therm}}$	$\Delta_{\mathrm{bind}}H$
pyrrole	trimethylamine	–34.81	3.35	10.14	–31.24
formic acid	formic acid	–67.46	7.42	8.49	–61.47
acetic acid	acetic acid	–70.13	5.41	9.98	–64.66
acrylic acid	acrylic acid	–72.17	5.01	10.13	–66.94
trifluoroacetic acid	trifluoroacetic acid	–65.34	5.08	10.30	–59.88
trifluoroacetic acid	cyclopentanone	–54.41	4.09	11.40	–48.84
trifluoroacetic acid	acetone	–51.59	4.74	13.28	–43.49
trifluoroacetic acid	dimethyl ether	–64.33	5.17	11.16	–57.91
trifluoroacetic acid	diethyl ether	–68.38	5.11	11.20	–61.99
hydrogen cyanide	dimethyl ether	–25.91	3.59	9.89	–21.11
iodine	dimethyl sulfide	–42.46	3.09	10.03	–38.01
iodine	diethyl sulfide	–45.68	3.18	10.02	–41.16
iodine	tetrahydrothiophene	–48.16	3.01	10.15	–43.68
iodine	benzene	–22.06	1.32	8.78	–20.65
iodine	diethyl ether	–33.25	2.99	10.27	–28.67
tetracyanoethylene	benzene	–38.58	4.13	12.26	–32.11
acetone	acetone	–27.56	3.76	11.87	–21.85
acetaldehyde	acetaldehyde	–19.17	2.69	12.71	–13.68
acetonitrile	acetonitrile	–26.09	2.77	12.35	–20.89
ammonia	ammonia	–12.73	6.02	10.09	–6.54
acetylene	ammonia	–14.75	4.93	8.36	–10.14
chloroform	ammonia	–21.47	4.72	11.39	–15.28
chloroform	sulfur dioxide	–14.54	2.15	13.02	–9.28
sulfur dioxide	*trans*-2-butene	–18.14	3.73	11.74	–12.58
dimethylamine	trimethylphosphine	–17.44	2.44	10.50	–14.41
methyl chloride	methyl chloride	–11.18	2.03	13.26	–5.81

Table S2

The comparison of the electronic binding energies computed in this work (DLPNO-CCSD(T1)/CBS(aug-cc-pVDZ, aug-cc-pVTZ)) with the literature values obtained using the same or higher level of theory. Unless otherwise stated, all values were calculated using the CCSD(T) method. The notation of basis sets is following: aXZ = aug-cc-pVXZ, aCXZ = aug-cc-pCVXZ. All values are given in kJ·mol^{-1}.

Compound A	Compound B	Ref.	Basis set	*BE* (lit.)	*BE* (this work)	Δ[a]
water	water	[1]	CBS(aQZ,a5Z) [b]	–21.01	–21.13	–0.12
		[2]	CBS(aQZ,a5Z)	–21.00		–0.13
		[3]	aQZ	–20.94		–0.19
		[4]	CBS(aTZ,aQZ)	–21.21		0.08
		[5]	CBS(aTZ,aQZ)	–20.59		–0.54
		[6]	CBS(aTZ,aQZ)	–20.96		–0.17
		[7]	CBS(a5Z,a6Z)	–20.87		–0.26
water	dimethyl ether	[8]	CBS(aDZ,aTZ)	–23.91	–24.67	–0.76
hydrogen fluoride	hydrogen fluoride	[9]	CBS(aCQZ, aC5Z, aC6Z)	–19.18	–19.16	0.02
hydrogen fluoride	water	[10]	a5Z	–36.40	–36.32	0.08
methanol	methanol	[5]	CBS(aTZ,aQZ)	–24.10	–24.01	0.09
		[6]	CBS(aTZ,aQZ)	–24.48		0.47
		[11]	CBS(aTZ,aQZ)	–24.47		0.46
methanol	methylamine	[5]	CBS(aTZ,aQZ)	–31.59	–31.45	0.14
		[6]	CBS(aTZ,aQZ)	–32.09		0.64
ethanol	ethanol	[11]	CBS(aDZ,aTZ)	–28.47	–27.46	1.01
1-propanol	1-propanol	[11]	CBS(aDZ,aTZ)	–29.94	–30.97	–1.03
formic acid	formic acid [d]	[12]	CBS(aQZ,a5Z)	–65.06	–67.46	–2.40
		[2]	CBS(aQZ,a5Z)	*–77.86*		*10.40*
		[3]	aTZ	*–78.45*		*10.99*
		[4]	CBS(aTZ,aQZ)	*–78.70*		*11.24*
		[7]	CBS(aQZ,a5Z)	*–78.46*		*11.00*
		[11]	CBS(aTZ,aQZ)	*–78.38*		*10.92*
acetic acid	acetic acid [d]	[13]	CBS(aTZ,aQZ,a5Z)	–70.92	–70.13	0.79
		[5]	CBS(aTZ,aQZ)	*–79.87*		*9.74*
		[6]	CBS(aTZ,aQZ)	*–81.21*		*11.08*
		[11]	CBS(aDZ,aTZ)	*–80.82*		*10.69*
acetone	acetone	[11]	CBS(aDZ,aTZ)	–28.88	–27.56	1.32
acetaldehyde	acetaldehyde	[11]	CBS(aTZ,aQZ)	–21.62	–19.17	2.45
ammonia	ammonia	[2]	CBS(aQZ,a5Z)	–13.26	–12.73	0.53
		[3]	aQZ	–13.16		0.43
		[4]	CBS(aTZ,aQZ)	–13.18		0.45
		[7]	CBS(aQZ,a5Z)	–13.11		0.38

[a] The difference *BE* (this work) – *BE* (lit.).

[b] Calculated using CCSD(T)-F12b.

[c] Calculated using DLPNO-CCSD(T).

[d] The deviations of 9-11 kJ·mol^{-1} for Refs. [2-7, 11] are likely caused by the insufficient optimization of the monomer and by the approximation of the CCSD(T) correlation effects with MP2, as shown for formic acid by Kalescky et al. [12]

Table S3

The comparison of the electronic binding energies computed in this work using different theory levels: "regular" – DLPNO-CCSD(T1)/CBS(aug-cc-pVDZ, aug-cc-pVTZ) with frozen core (FC) approximation, and "benchmark" – DLPNO-CCSD(T1)/CBS(aug-cc-pVTZ, aug-cc-pVQZ) with Douglas–Kroll (DK) approach for the treatment of relativistic effects and no FC approximation (except iodine atoms). All values are given in kJ·mol^{-1}.

Compound A	Compound B	*BE*		Δ[a]
		regular	benchmark	
water	water	–21.13	–20.70	–0.43
water	dimethyl ether	–24.67	–24.24	–0.43
hydrogen fluoride	hydrogen fluoride	–19.16	–18.92	–0.24
hydrogen fluoride	water	–36.32	–36.42	0.10
hydrogen fluoride	dimethyl ether	–42.81	–42.40	–0.41
hydrogen fluoride	diethyl ether	–46.40	–45.56	–0.84
methanol	methanol	–24.01	–23.69	–0.32
methanol	methylamine	–31.45	–30.88	–0.57
formic acid	formic acid	–67.46	–67.44	–0.02
acetic acid	acetic acid	–70.13	–69.74	–0.39
iodine	dimethyl sulfide	–42.46	–41.11	–1.35
iodine	diethyl sulfide	–45.68	–47.26	1.58
iodine	diethyl ether	–33.25	–33.97	0.72
acetone	acetone	–27.56	–27.15	–0.41
acetaldehyde	acetaldehyde	–19.17	–19.04	–0.13
acetonitrile	acetonitrile	–26.09	–25.96	–0.13
ammonia	ammonia	–12.73	–13.03	0.30
chloroform	ammonia	–21.47	–22.04	0.57
methyl chloride	methyl chloride	–11.18	–11.77	0.59

[a] The difference *BE* (regular) – *BE* (benchmark).

Table S4

The binding entropies computed in this work (QC) and derived from the experimental Gibbs energies (lit). All values are given in $J \cdot K^{-1} \cdot mol^{-1}$.

Compound A	Compound B	ΔG (lit)[a]	ΔS_{trans} (QC)	ΔS_{rot} (QC)	ΔS_{vib} (QC)	ΔS_{vib} [b]	ΔS (QC)	ΔS [c]
water	water	7.4	–136.2	0.7	52.6	63.4	–82.8	–72.1
		8.2				60.7		–74.8
		7.9				61.7		–73.8
water	dimethyl ether	7.8	–140.7	–28.8	72.3	84.7	–97.2	–84.9
hydrogen fluoride	hydrogen fluoride	10.3	–137.5	28.1	24.7	24.7	–84.6	–84.6
hydrogen fluoride	water	2.3	–136.8	14.0	25.0	16.6	–97.8	–106.2
hydrogen fluoride	dimethyl ether	−6.5	–141.6	–12.9	46.7	56.8	–107.8	–97.7
hydrogen fluoride	methyl ethyl ether	−7.4	–142.5	–17.3	46.0	55.9	–113.8	–103.9
hydrogen fluoride	diethyl ether	−5.7	–143.1	–19.2	46.7	50.4	–115.6	–111.9
hydrogen chloride	dimethyl ether	3.8	–146.3	–13.9	54.3	67.9	–105.9	–92.4
methanol	methanol	8.5	–143.3	–51.4	95.6	108.7	–99.1	–86.0
		7.1				113.4		–81.3
		8.0				110.4		–84.3
		6.7				114.7		–80.0
		7.0				113.7		–81.0
methanol	methylamine	1.6	–143.1	–52.6	90.5	108.4	–105.3	–87.4
methanol	dimethylamine	1.3	–145.3	–59.9	99.0	112.5	–106.2	–92.7
methanol	trimethylamine	0.4	–146.6	–64.6	85.1	108.4	–126.1	–102.8
		1.0				106.4		–104.8
methanol	triethylamine	−0.3	–148.6	–71.7	99.7	123.1	–120.5	–97.2
ethanol	ethanol	6.6	–147.9	–69.6	97.1	126.9	–120.3	–90.6
		4.9				132.6		–84.9
1-propanol	1-propanol	5.0	–151.2	–79.7	99.8	132.9	–131.0	–97.9
2-propanol	2-propanol	3.0	–151.2	–80.5	125.3	145.8	–106.4	–85.9
		5.8				136.4		–95.3
		5.5				137.4		–94.3
2-butanol	2-butanol	4.6	–153.8	–87.8	89.9	142.5	–151.7	–99.1
tert-butyl alcohol	*tert*-butyl alcohol	3.0	–153.8	–85.8	90.3	138.6	–149.3	–101.1
		4.5				133.5		–106.1
trifluoroethanol	methanol	0.3	–148.5	–68.0	72.2	115.2	–144.3	–101.3
trifluoroethanol	trifluoroethanol	3.5	–157.5	–89.8	113.6	152.7	–133.7	–94.7
trifluoroethanol	propanal	0.7	–153.7	–83.8	105.9	133.2	–131.6	–104.3
trifluoroethanol	diethyl ether	−0.5	–155.5	–88.2	124.7	150.1	–119.0	–93.6
trifluoroethanol	acetone	−2.0	–153.7	–84.6	97.8	133.5	–140.5	–104.8
trifluoroethanol	tetrahydrofuran	−3.0	–155.3	–85.7	95.9	131.2	–145.2	–109.8
trifluoroethanol	ammonia	−2.1	–142.1	–40.5	74.5	83.8	–108.1	–98.8
trifluoroethanol	pyridine	−5.1	–156.0	–86.0	121.6	133.8	–120.3	–108.2
trifluoroethanol	trimethylamine	−6.8	–153.8	–85.0	104.1	120.9	–134.7	–118.0
trifluoroethanol	triethylamine	−6.1	–157.6	–95.1	102.8	125.3	–149.8	–127.3
trifluoroethanol	tetramethylguanidine	−12.6	–158.4	–95.1	80.1	122.1	–173.4	–131.4
hexafluoro-2-propanol	methanol	−2.7	–149.8	–72.9	94.6	120.5	–128.1	–102.2
hexafluoro-2-propanol	diethyl ether	−4.6	–157.9	–95.1	126.0	150.8	–127.0	–102.2

Compound A	Compound B	ΔG (lit)[a]	ΔS_{trans} (QC)	ΔS_{rot} (QC)	ΔS_{vib} (QC)	ΔS_{vib} [b]	ΔS (QC)	ΔS [c]
hexafluoro-2-propanol	acetone	−5.8	–155.7	–90.2	96.4	148.3	–149.5	–97.5
hexafluoro-2-propanol	tetrahydrofuran	−7.8	–157.6	–91.4	92.0	139.8	–157.0	–109.3
hexafluoro-2-propanol	ammonia	−7.9	–142.9	–43.9	74.4	82.0	–112.4	–104.8
hexafluoro-2-propanol	trimethylamine	−14.4	–155.9	–91.1	72.9	110.4	–174.1	–136.5
hexafluoro-2-propanol	triethylamine	−12.5	–160.4	–102.4	95.7	123.2	–167.1	–139.6
perfluoro-*tert*-butanol	diethyl ether	−8.3	–159.0	–98.2	82.7	137.5	–174.5	–119.7
perfluoro-*tert*-butanol	acetone	−9.4	–156.7	–92.3	97.8	143.1	–151.2	–105.9
perfluoro-*tert*-butanol	tetrahydrofuran	−12.5	–158.8	–93.8	60.2	121.1	–192.4	–131.6
perfluoro-*tert*-butanol	ammonia	−13.3	–143.2	–45.1	75.2	76.5	–113.2	–111.9
perfluoro-*tert*-butanol	trimethylamine	−21.8	–156.8	–93.4	107.1	112.2	–143.2	–138.1
pyrrole	trimethylamine	0.0	–151.7	–78.2	102.7	125.2	–127.3	–104.8
formic acid	formic acid	−14.6	–147.9	–62.9	57.1	53.5	–153.6	–157.2
		−14.5				53.2		–157.5
acetic acid	acetic acid	−17.7	–151.2	–78.9	79.5	72.6	–150.6	–157.5
		−18.7				76.0		–154.1
		−18.6				75.6		–154.5
acrylic acid	acrylic acid	−22.2	–153.4	–84.9	83.7	88.3	–154.6	–150.0
trifluoroacetic acid	trifluoroacetic acid	−19.7	–159.2	–91.3	85.0	115.7	–165.4	–134.7
trifluoroacetic acid	cyclopentanone	−12.9	–157.1	–89.6	101.5	126.2	–145.2	–120.5
trifluoroacetic acid	acetone	−13.4	–154.3	–85.2	115.8	138.6	–123.7	–100.9
trifluoroacetic acid	dimethyl ether	−23.9	–152.3	–79.2	94.7	117.4	–136.8	–114.1
trifluoroacetic acid	diethyl ether	−20.4	–156.2	–89.7	100.3	106.4	–145.6	–139.5
hydrogen cyanide	dimethyl ether	5.1	–144.1	19.4	48.8	36.9	–76.0	–87.9
iodine	dimethyl sulfide	−5.4	–157.6	–50.1	82.6	98.3	–125.1	–109.4
iodine	diethyl sulfide	−8.5	–161.1	–55.4	83.0	106.8	–133.6	–109.7
iodine	tetrahydrothiophene	−11.3	–160.9	–54.6	86.0	107.0	–129.5	–108.5
iodine	benzene	4.2	–159.8	–33.5	81.9	109.9	–111.3	–83.3
iodine	diethyl ether	3.4	–159.2	–54.6	89.3	106.3	–124.6	–107.5
tetracyanoethylene	benzene	−1.7	–157.2	–77.3	108.6	132.5	–125.9	–102.0
acetone	acetone	5.9	–150.8	–81.3	89.2	138.8	–142.9	–93.2
acetaldehyde	acetaldehyde	8.9	–147.3	–66.2	114.7	137.7	–98.8	–75.7
acetonitrile	acetonitrile	3.8	–146.4	–58.2	106.7	121.9	–98.0	–82.8
ammonia	ammonia	15.0	–135.5	–3.4	78.6	66.7	–60.3	–72.2
acetylene	ammonia	9.8	–137.8	–3.3	59.8	74.3	–81.3	–66.9
chloroform	ammonia	9.3	–142.4	–31.5	104.9	91.6	–69.0	–82.3
chloroform	sulfur dioxide	10.6	–155.3	–71.1	126.8	159.7	–99.6	–66.7
sulfur dioxide	*trans*-2-butene	5.2	–151.1	–65.3	95.2	156.8	–121.2	–59.6
dimethylamine	trimethylphosphine	11.0	–150.4	–76.0	95.0	141.2	–131.4	–85.2
methyl chloride	methyl chloride	15.3	–149.0	–50.4	132.6	128.8	–66.8	–70.6

[a] The experimental Gibbs energies of gas-phase molecular complexation.

[b] Calculated as ΔS(lit) – (ΔS_{trans}(QC) + ΔS_{rot}(QC)).

[c] Calculated from the experimental Gibbs energies (column 3) and computed binding enthalpies.

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