Supporting Information

Gaseous Phase Heat Capacity of Benzoic Acid

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Table S2 – Calculated molar gaseous phase heat capacities, $C_{p,\mathrm{m}}$, obtained for acetic acid (CH3COOH) at constant pressure, derived from the calculated frequencies after anharmonicity correction using the scaling factors presented in Table 1. The methyl and O-H rotations were treated as hindered rotors using the approach proposed by Ayala and Schlegel [(#)] incorporated in Gaussian 03 software package.

Temperature / K	298.15	300	400	500	600
	C_p / ($J \cdot K^{-1} \cdot mol^{-1}$)				
B3LYP / 6-311++G(d,p)	66.5	66.8	81.7	94.8	105.7
BLYP / 6-311++G(d,p)	66.7	67.0	82.0	95.1	105.9
BP86 / 6-311++G(d,p)	66.7	67.0	82.1	95.1	106.0
MP2 / 6-311++G(d,p)	66.7	67.0	82.1	95.1	106.0
B3LYP / cc-pvtz	66.5	66.8	81.8	94.9	105.8
BLYP / cc-pvtz	66.7	67.0	82.0	95.0	105.9
BP86 / cc-pvtz	66.6	66.9	82.0	95.0	105.9
B3LYP / TZVP	66.3	66.6	81.6	94.6	105.6
BLYP / TZVP	66.5	66.8	81.8	94.9	105.7
BP86 / TZVP	66.6	66.9	81.9	95.0	105.9

Ayala, P. Y.; Schlegel, H. B. Identification and treatment of internal rotation in normal mode vibrational analysis. *J. Chem. Phys.* **1998**, *108*, 2314-2325

Table S3 – Calculated molar gaseous phase heat capacities, $C_{p,\mathrm{m}}$, obtained for formic acid (HCOOH) at constant pressure, derived from the calculated frequencies after anharmonicity correction using the scaling factors presented in Table 1.

Temperature /K	298.15	300	400	500	600
	C_p / ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)				
B3LYP / 6-311++G(d,p)	45.4	45.5	53.9	61.4	67.5
BLYP / 6-311++G(d,p)	45.6	45.7	54.3	61.7	67.9
BP86 / 6-311++G(d,p)	45.5	45.6	54.1	61.6	67.7
MP2 / 6-311++G(d,p)	45.7	45.8	54.2	61.7	67.8
B3LYP / cc-pvtz	45.3	45.5	53.9	61.3	67.5
BLYP / cc-pvtz	45.5	45.7	54.2	61.6	67.8
BP86 / cc-pvtz	45.4	45.5	54.0	61.5	67.6
B3LYP / TZVP	45.3	45.4	53.8	61.2	67.4
BLYP / TZVP	45.5	45.6	54.1	61.6	67.7
BP86 / TZVP	45.4	45.5	54.0	61.5	67.6

Table S4 – Calculated molar gaseous phase heat capacities, $C_{p,m}$, obtained for benzene (C_6H_6) at constant pressure, derived from the calculated frequencies after anharmonicity correction using the scaling factors presented in Table 1.

Temperature /K	298.15	300	400	500	600
	C_p / ($J \cdot K^{-1} \cdot mol^{-1}$)				
B3LYP / 6-311++G(d,p)	83.4	84.0	114.4	140.1	160.6
BLYP / 6-311++G(d,p)	83.4	84.0	114.4	140.1	160.6
BP86 / 6-311++G(d,p)	83.9	84.5	114.9	140.5	160.9
MP2 / 6-311++G(d,p)	87.2	87.8	116.3	140.0	159.0
B3LYP / cc-pvtz	83.1	83.7	114.1	139.8	160.4
BLYP / cc-pvtz	83.0	83.6	114.0	139.7	160.3
BP86 / cc-pvtz	83.2	83.8	114.2	139.8	160.3
B3LYP / TZVP	83.5	84.1	114.5	140.1	160.6
BLYP / TZVP	83.5	84.1	114.5	140.1	160.5
BP86 / TZVP	84.2	84.8	115.1	140.6	161.0

Table S5 – Calculated molar gaseous phase heat capacities, $C_{p,\mathrm{m}}$, obtained for toluene ($C_6H_5CH_3$) at constant pressure, derived from the calculated frequencies after anharmonicity correction using the scaling factors presented in Table 1. "-CH_3" rotor was treated as a free rotor.

Temperature /K	298.15	300	400	500	600
	C_p / ($J \cdot K^{-1} \cdot mol^{-1}$)				
B3LYP / 6-311++G(d,p)	105.1	105.8	141.5	172.3	197.5
BLYP / 6-311++G(d,p)	105.2	105.9	141.5	172.2	197.4
BP86 / 6-311++G(d,p)	105.8	106.5	142.1	172.8	197.9
MP2 / 6-311++G(d,p)	109.2	109.9	145.3	175.6	200.2
B3LYP / cc-pvtz	104.9	105.6	141.3	172.1	197.3
BLYP / cc-pvtz	104.9	105.6	141.2	172.0	197.2
BP86 / cc-pvtz	105.2	105.9	141.5	172.2	197.4
B3LYP / TZVP	105.2	105.9	141.5	172.2	197.4
BLYP / TZVP	105.3	106.0	141.5	172.2	197.2
BP86 / TZVP	106.0	106.7	142.3	172.9	197.9

Table S6 – Calculated molar gaseous phase heat capacities, $C_{p,m}$, obtained for ethane (C_2H_6) at constant pressure, derived from the calculated frequencies after anharmonicity correction using the scaling factors presented in Table 1. The methyl group was treated as hindered rotor using the approach proposed by Ayala and Schlegel (#), incorporated in Gaussian 03 software package.

Temperature /K	298.15	300	400	500	600
	C_p / ($J \cdot K^{-1} \cdot mol^{-1}$)				
B3LYP / 6-311++G(d,p)	53.2	53.5	66.5	78.6	89.6
BLYP / 6-311++G(d,p)	53.2	53.5	66.1	78.2	89.1
BP86 / 6-311++G(d,p)	53.5	53.7	66.6	78.7	89.6
MP2 / 6-311++G(d,p)	53.6	53.8	66.6	78.7	89.7
B3LYP / cc-pvtz	53.3	53.6	66.2	78.3	89.2
BLYP / cc-pvtz	53.5	53.8	66.6	78.7	89.6
BP86 / cc-pvtz	53.4	53.6	66.3	78.4	89.4
B3LYP / TZVP	53.1	53.4	66.0	78.0	88.9
BLYP / TZVP	53.4	53.6	66.4	78.5	89.4
BP86 / TZVP	53.5	53.7	66.6	78.8	89.7

(#) Ayala, P. Y.; Schlegel, H. B. Identification and treatment of internal rotation in normal mode vibrational analysis. *J. Chem. Phys.* **1998**, *108*, 2314-2325

Table S7 – Calculated molar gaseous phase heat capacities, $C_{p,\mathrm{m}}$, obtained for methane (CH_4) at constant pressure, derived from the calculated frequencies after anharmonicity correction using the scaling factors presented in Table 1.

Temperature /K	298.15	300	400	500	600
	C_p / ($J \cdot K^{-1} \cdot mol^{-1}$)				
B3LYP / 6-311++G(d,p)	35.7	35.8	40.7	46.6	52.5
BLYP / 6-311++G(d,p)	35.7	35.7	40.5	46.4	52.2
BP86 / 6-311++G(d,p)	35.8	35.9	40.8	46.7	52.6
MP2 / 6-311++G(d,p)	35.8	35.8	40.8	46.7	52.6
B3LYP / cc-pvtz	35.8	35.8	40.7	46.6	52.5
BLYP / cc-pvtz	35.7	35.7	40.6	46.4	52.2
BP86 / cc-pvtz	35.8	35.9	40.8	46.7	52.5
B3LYP / TZVP	35.7	35.8	40.6	46.5	52.4
BLYP / TZVP	35.6	35.7	40.4	46.2	52.1
BP86 / TZVP	35.8	35.8	40.7	46.6	52.4

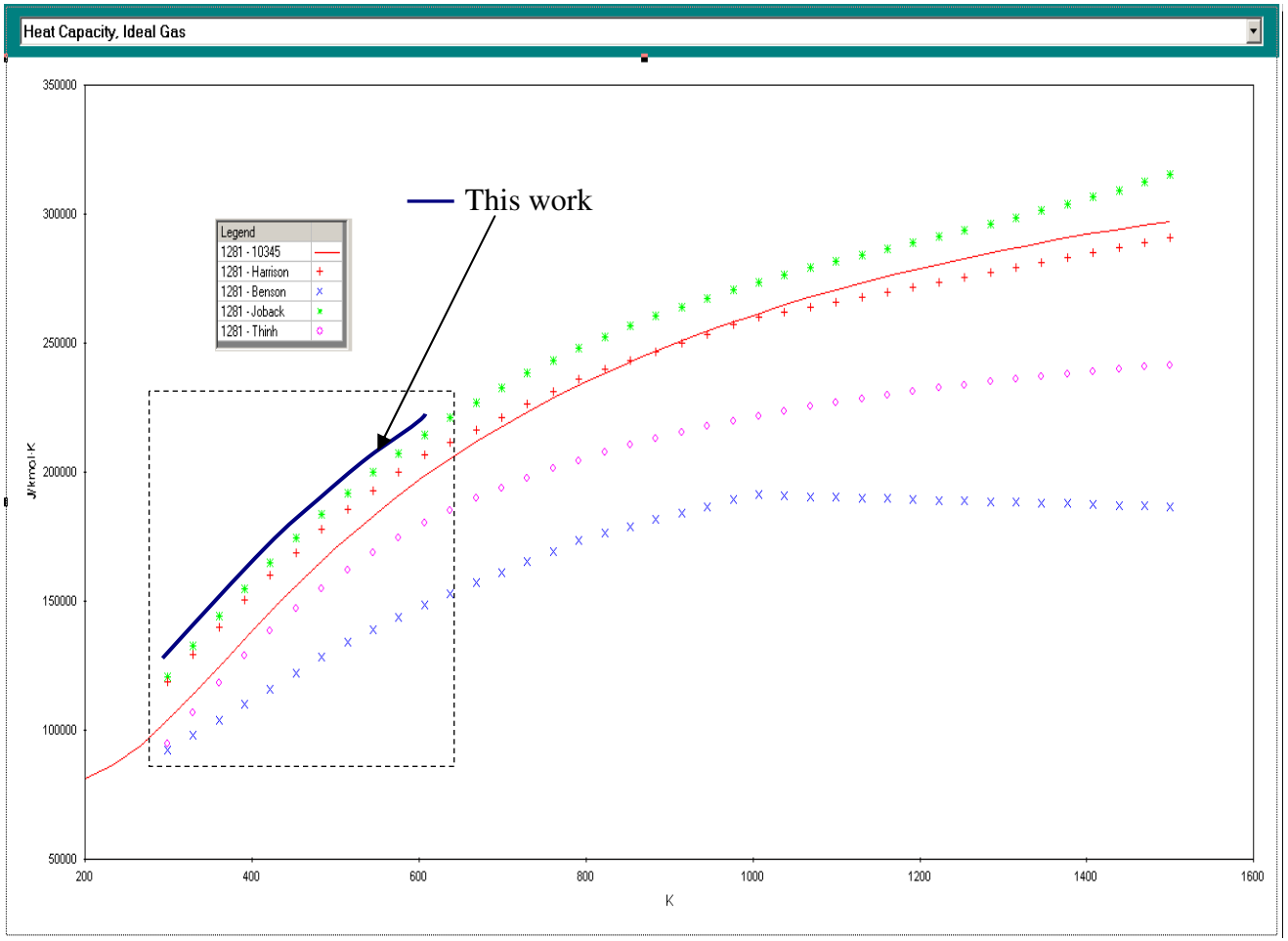

Figure S1 – Estimated molar gaseous phase heat capacities, $C_{p,\mathrm{m}}$, obtained for benzoic acid at constant pressure, using several estimation procedure. The gaseous phase heat capacities, $C_{p,\mathrm{m}}$ are underestimated by all the estimative methods.