Electronic supporting information:

Dissecting intermolecular interactions in the condensed phase of ibuprofen and related compounds: The specific role and quantification of hydrogen bonding and dispersion forces

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Table S1

Provenance, purity, methods of purification and analysis of chemicals used in this work.

Compound	CAS	Source	Initial purity	Final purity [a]
(±)-ibuprofen	15687-27-1	Alfa	99%	0.999
(±)-2-phenylpropionic acid	492-37-5	Alfa	98%	0.999
(±)-α-methyl-4-(2-methylpropyl) -benzeneacetic acid methyl ester	61566-34-5	Fisher	98%	0.999

[a] Purification was performed by the fractional distillation in vacuum for the liquids and fractional sublimation for solids. Mass fraction impurity was determined by the gas chromatography.

Table S2
Results of transpiration method: absolute vapor pressures p_{sat}, standard molar vaporization enthalpies and standard molar vaporization entropies

T/ K[a]	m/ mg[b]	$V(N_2)$[c] / dm^3	T_a/ K[d]	Flow/ $dm^3 \cdot h^{-1}$	p_{sat}/ Pa[e]	$u(p_{sat})$/ Pa[f]	$\Delta_l^g H_m^o$ $kJ \cdot mol^{-1}$	$\Delta_l^g S_m^o$ $J \cdot K^{-1} \cdot mol^{-1}$
(±)-ibuprofene: $\Delta_l^g H_m^o(298.15\ K) = (89.4 \pm 0.8)\ kJ \cdot mol^{-1}$								
$\ln(p/p^\circ) = \frac{370.8}{R} - \frac{122629.4}{RT} - \frac{111.6}{R} \ln\frac{T}{298.15}$								
355.4	0.80	4.553	296.3	4.97	2.11	0.06	82.97	144.0
359.2	1.03	4.363	297.2	4.94	2.82	0.08	82.54	142.7
360.9	1.31	4.894	298.2	4.89	3.23	0.09	82.35	142.2
362.7	1.00	3.293	297.1	4.94	3.64	0.10	82.15	141.5
364.9	1.26	3.513	298.4	4.90	4.33	0.11	81.91	140.9
367.0	1.01	2.436	297.2	5.04	4.98	0.13	81.67	140.2
368.9	1.38	2.849	298.9	4.88	5.83	0.17	81.46	139.8
372.8	1.55	2.412	299.2	4.82	7.74	0.22	81.02	138.6
375.2	1.02	1.339	297.3	5.02	9.14	0.25	80.75	137.9
376.8	3.09	3.699	299.3	4.93	10.08	0.28	80.57	137.3
(±)-2-phenylpropionic acid: $\Delta_l^g H_m^o(298.15\ K) = (82.5 \pm 1.0)\ kJ \cdot mol^{-1}$								
$\ln(p/p^\circ) = \frac{320.6}{R} - \frac{106397.8}{RT} - \frac{81.0}{R} \ln\frac{T}{298.15}$								
353.6	0.91	5.434	295.9	4.53	2.01	0.06	77.76	130.0
357.0	0.77	3.470	295.9	4.34	2.63	0.07	77.48	129.4
361.6	0.99	3.180	295.9	4.34	3.70	0.10	77.11	128.4
366.6	1.59	3.759	295.9	4.34	5.05	0.15	76.71	127.0
371.5	3.48	5.855	295.9	4.34	7.08	0.20	76.31	126.0
375.5	1.52	1.952	295.9	4.34	9.27	0.26	75.98	125.1
377.2	0.93	1.048	295.9	4.34	10.56	0.29	75.84	124.9
(±)-α-methyl-4-(2-methylpropyl)-benzeneacetic acid methyl ester: $\Delta_l^g H_m^o(298.15\ K) = (69.5 \pm 0.3)\ kJ \cdot mol^{-1}$								
$\ln(p/p^\circ) = \frac{343.0}{R} - \frac{103464.5}{RT} - \frac{114.6}{R} \ln\frac{T}{298.15}$								
298.1	2.69	47.763	291.6	4.03	0.62	0.02	69.46	133.4
303.7	0.97	10.398	292.4	4.03	1.03	0.03	68.81	131.0
309.9	1.35	8.385	292.0	4.03	1.77	0.05	68.11	128.9
316.7	0.87	3.086	292.4	4.03	3.12	0.08	67.33	126.4
323.0	2.80	6.239	292.2	4.03	4.95	0.13	66.62	123.8
328.6	1.00	1.444	293.4	4.13	7.67	0.22	65.98	122.0
334.3	1.16	1.101	293.3	4.13	11.62	0.32	65.32	120.1
340.0	1.59	1.032	293.2	4.13	17.10	0.45	64.68	118.1
345.9	4.19	1.788	292.8	4.13	25.90	0.67	64.00	116.4
353.4	3.83	1.032	293.8	4.13	41.14	1.05	63.15	113.9
359.0	6.74	1.307	293.8	4.13	57.17	1.45	62.51	112.1

[a] Saturation temperature ($u(T) = 0.1$ K). [b] Mass of transferred sample condensed at $T = 273$ K. [c] Volume of nitrogen ($u(V) = 0.005\ dm^3$) used to transfer m ($u(m) = 0.0001$ g) of the sample. [d] T_a is the temperature of the soap bubble meter used for measurement of the gas flow. [e] Vapor

pressure at temperature *T*, calculated from the *m* and the residual vapor pressure at the condensation temperature calculated by an iteration procedure. [f] Uncertainties were calculated with $u(p_{sat}/Pa) = 0.005 + 0.025(p_{sat}/Pa)$ for pressures below 5 Pa and with $u(p_{sat}/Pa) = 0.025 + 0.025(p_{sat}/Pa)$ for pressure from 5 to 3000 Pa. The uncertainties for *T, V, p, m* are standard uncertainties with 0.95 confidence level. Uncertainty of the vaporization enthalpy $U(\Delta_l^g H_m^o)$ is the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [1-3].

TABLE S3

Compilation of data on molar heat capacities $C^{o}_{p,m}$ and differences $\Delta^{g}_{l,cr}C^{o}_{p,m}$, in J·K^{-1}·mol^{-1}, at 298.15 K.

compound	$C^{o}_{p,m}$(liq) [a]	$-\Delta^{g}_{l}C^{o}_{p,m}$ [b]	$C^{o}_{p,m}$(cr) [a]	$-\Delta^{g}_{cr}C^{o}_{p,m}$ [b]
(±)-ibuprofen	388.6	111.6	293.0	44.7
(±)-2-phenylpropionic acid	271.0	81.0	-	-
(±)-α-methyl-4-(2-methylpropyl) -benzeneacetic acid methyl ester	398.0	114.1	320.5	48.8

[a] Calculated according to the procedure developed by Chickos *et al.*[4].

[b] Calculated according to the procedure developed by Chickos and Acree [5].

In this work the fusion enthalpy of (±)-ibuprofen at T_{fus} K (see Table S4 has been adjusted to the reference temperature T = 298.15 K. The adjustment was calculated with help of Eq. (6) [5]:

$$\Delta^{l}_{cr}H^{o}_{m}(298.15\ K)/(J\cdot mol^{-1}) = \Delta^{l}_{cr}H^{o}_{m}(T_{fus}/K) - (\Delta^{g}_{cr}C^{o}_{p,m}-\Delta^{g}_{l}C^{o}_{p,m})\times[(T_{fus}/K) - 298.15\ K], \quad (6)$$

where $\Delta^{g}_{cr}C^{o}_{p,m}$ and $\Delta^{g}_{l}C^{o}_{p,m}$ were taken from table S3. With this adjustment, the molar enthalpy of fusion, $\Delta^{l}_{cr}H^{o}_{m}$(298.15 K) of (±)-ibuprofen was calculated and used for calculations of sublimation enthalpies according to the general equation:

$\Delta^{g}_{cr}H^{o}_{m}(298.15\ K) = \Delta^{g}_{l}H^{o}_{m}(298.15\ K) + \Delta^{l}_{cr}H^{o}_{m}(298.15\ K) = 89.4+21.6 = 111.0\pm1.1$ kJ·mol^{-1}.(see Table S4)

Table S4 Phase transition enthalpies of (±)-ibuprofen (in kJ·mol^{-1}).

Compounds	T_{fus}/K	$\Delta^{l}_{cr}H^{o}_{m}$ at T_{fus}	$\Delta^{l}_{cr}H^{o}_{m}$ [a]	$\Delta^{g}_{l}H^{o}_{m}$ [b]	$\Delta^{g}_{cr}H^{o}_{m}$ [c]
			298.15 K		
(±)-ibuprofen	348.4±0.1	25.0±0.1 [6]	21.6±1.1	89.4±0.8	111.0±1.1

[a] The experimental enthalpies of fusion $\Delta^{l}_{cr}H^{o}_{m}$ measured at T_{fus} and adjusted to 298 K according to procedure developed by Chickos and Acree [5].

[b] From Table S2

[c] Calculated as the difference between column 5 and 4 in this table.

TABLE S5. Compilation of data on enthalpies of vaporization $\Delta_l^g H_m^o$(298.15 K) of alkyl acetates, in kJ·mol^{-1}

	$\Delta_l^g H_m^o$(298.15 K) [a]
Methyl acetate	32.3±0.2
Ethyl acetate	35.6±0.2
Propyl acetate	39.1±0.2
Butyl acetate	43.6±0.2
Pentyl acetate	48.6±0.4
Hexyl acetate	51.9±0.3
Heptyl acetate	57.1±0.2
Octyl acetate	60.7±0.4
Nonyl acetate	66.2±0.2
Decyl acetate	70.2±0.3
Undecyl acetate	75.1±0.3
Dodecyl acetate	79.6±0.3
Tridecyl acetate	84.7±0.5
Tetradecyl acetate	89.9±0.2
Hexadecyl acetate	98.1±0.5
Octadecyl acetate	107.2±0.5

[a] Data from [7]

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