

Supporting Information for “How important is thermal expansion for predicting molecular crystal structures and thermochemistry at finite temperatures?”

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Contents

1	Convergence tests	2
1.1	Lattice dynamics supercell size	2
1.2	Grüneisen parameter finite difference	2
2	Empirical Thermochemical data	3
2.1	Empirical Entropy Data for Carbon Dioxide	3
2.2	Empirical Entropy Data for Ice	5
2.3	Empirical Enthalpy and Entropy Data for Acetic Acid	7
2.4	Empirical Enthalpy Data for Imidazole	10

This supporting information provides data from convergence tests on the lattice dynamics supercell size and the Grüneisen parameter finite difference step size. It also includes details of the empirical enthalpy and entropy data derived from experimental data for crystalline carbon dioxide (phase I), ice Ih, acetic acid (orthorhombic polymorph), and imidazole (α polymorph).

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1 Convergence tests

1.1 Lattice dynamics supercell size

The lattice dynamics calculations reported in the main paper were performed using a $3 \times 3 \times 3$ supercell. For carbon dioxide, using a larger $5 \times 5 \times 5$ supercell has trivial impact on the Helmholtz vibrational free energy. For the minimum electronic energy structure, the vibrational free energy per molecule changes by only 0.001 kJ/mol at 0 K up to 0.04 kJ/mol at 210 K. These changes are much smaller than the other errors in the predicted thermochemical quantities, indicating that the lattice dynamics supercell calculations are sufficiently converged.

1.2 Grüneisen parameter finite difference

The mode-specific Grüneisen parameters were computed via finite difference of the phonon frequencies in unit cells which were isotropically expanded and contracted by 10 \AA^3 . The resulting Helmholtz vibrational free energy contribution is not particularly sensitive to the finite difference step size. Figure S1a plots the differences in the carbon dioxide Helmholtz vibrational free energy as a function of the step size. Using either an 8 \AA^3 or 12 \AA^3 step size instead of a 10 \AA^3 one in the finite difference alters the vibrational free energy by less than 0.05 kJ/mol per molecule over the relevant volume range.

Similar results are obtained for acetic acid (Figure S1b). The difference in vibrational free energies obtained by using an 8 \AA^3 step size instead of a 10 \AA^3 one is ~ 0.01 kJ/mol per molecule in the relevant volume range of 44-48 $\text{cm}^3/\text{molecule}$. A 12 \AA^3 step size appears to be slightly too large for the finite difference in acetic acid, since it changes the vibrational free energy by up to ~ 0.1 kJ/mol per molecule over the relevant volume range.

In other words, the impact of the finite difference step size used here on the predicted enthalpies and free energies is 1–2 orders of magnitude smaller than the errors in the experimental enthalpies/free energies. Note that for crystals which expand anisotropically, it might be preferable to use an alternative scheme in the finite difference (e.g. perhaps performing finite difference over several different external pressures).

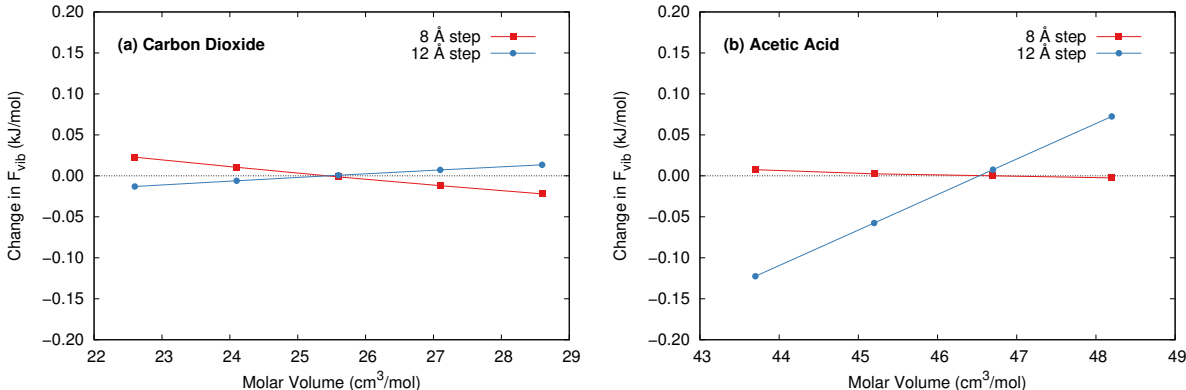


Figure S1: Change in the crystalline (a) carbon dioxide and (b) acetic acid Helmholtz vibrational free energy upon using an isotropic 8 \AA^3 or 12 \AA^3 finite difference step size instead of a 10 \AA^3 one when computing the MP2/aTZ Grüneisen parameters.

2 Empirical Thermochemical data

2.1 Empirical Entropy Data for Carbon Dioxide

Experimental enthalpy of sublimation data for carbon dioxide (phase I) was taken from Azreg-Aïnou.¹ The empirical entropies for carbon dioxide were derived from experimental data according to:

$$\Delta S_{sub}^{empr}(T) = \Delta S_{sub}^{expt}(194.7K) - \int_{194.7K}^T \frac{C_{p,crystal}^{expt}(T)}{T} dT + (S_{gas}(T) - S_{gas}(194.7K)) \quad (1)$$

This expression computes the sublimation entropy at temperature T in terms of the sublimation entropy at the 194.7 K sublimation point plus corrections for how the entropy of the crystal and gas vary with temperature. The sublimation entropy at the sublimation point is 129.62 J/mol K, as reported by Giaque and Egan.²

The temperature dependence of the crystal entropy was computed via integration of the isobaric heat capacity data of Giaque and Egan.² They report C_p values up to 189.78 K. The C_p value at 194.7 K was linearly extrapolated to 55.51 J/mol K using the five highest temperature values reported by Giaque and Egan. The data was cubically splined and integrated using Mathematica.

The term $S_{gas}(T)$ was computed according to:

$$S_{gas} = S_{gas,trans} + S_{gas,rot} + S_{gas,vib} \quad (2)$$

$$S_{gas,trans} = R \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{\frac{3}{2}} \left(\frac{k_B T \exp\left(\frac{5}{2}\right)}{P} \right) \right] \quad (3)$$

$$S_{gas,rot} = R \ln \left(\frac{8\pi^2 e T I k_B}{\sigma h^2} \right) \quad \text{where } \sigma = 2 \quad (4)$$

$$S_{gas,vib} = N_A \sum_i \left(\frac{\hbar \omega_i}{T \left(\exp\left(\frac{\hbar \omega_i}{k_B T}\right) - 1 \right)} - k_B \ln \left[1 - \exp\left(-\frac{\hbar \omega_i}{k_B T}\right) \right] \right) \quad (5)$$

using the experimental rotational constant (0.39021 cm^{-1} , which corresponds to a moment of inertia of $7.17 \times 10^{-46} \text{ Hz}$)³ and vibrational frequencies (2349, 1333, 667, & 667 cm^{-1}).⁴ The final results are summarized in Table S1.

Table S1: Contributions to the empirical entropy of sublimation for phase I carbon dioxide, in J/mol K.

Temperature (K)	$S_{gas}(T)$	$\int_{194.7K}^T \frac{C_{p,crystal}^{expt}(T)}{T} dT$	$\Delta S_{sub}^{empr}(T)$
15	123.67	-68.32	122.6
20	132.04	-67.30	130.0
30	143.84	-63.77	138.2
40	152.21	-59.12	142.0
50	158.70	-54.07	143.4
60	164.01	-49.02	143.7
70	168.49	-44.12	143.3
80	172.38	-39.50	142.5
90	175.81	-35.14	141.6
100	178.89	-31.05	140.6
110	181.67	-27.16	139.5
120	184.23	-23.48	138.3
130	186.59	-19.97	137.2
150	190.88	-13.37	134.9
170	194.71	-7.21	132.6
190	198.20	-1.35	130.2
194.7	198.99	0.00	129.6

2.2 Empirical Entropy Data for Ice

Experimental enthalpy of sublimation data for ice Ih was taken from the equation of state developed by Feistel and Wagner.⁵ The empirical entropy of sublimation for ice Ih was determined using the following equation:

$$\begin{aligned} \Delta S_{sub}^{empr}(T) = & S_{gas}(T) - S_{gas}(373.15K) + \Delta S_{vap}(373.15K) \\ & + S_{liquid}(373.15K) - S_{liquid}(273.15K) + \Delta S_{fus}(273.15K) \\ & + \int_T^{273.15K} \frac{C_{p,solid}(T)}{T} dT \end{aligned} \quad (6)$$

The entropy of fusion used is 22.0 J/mol K. This was found by dividing the entropy of fusion (6.01 kJ/mol) at the freezing point (273.15 K) by the freezing point temperature. The entropy of vaporization used is 108.97 J/mol K. This was similarly found by dividing the enthalpy of vaporization (40.66 kJ/mol) at the boiling point (373.15 K) by the boiling point temperature. Both the entropy of fusion and vaporization cited above were taken from the Handbook of Chemistry and Physics.⁶ Entropies for the gas and liquid water are reported in the NIST/TRC Web Thermo Tables.⁷ The entropy of liquid water at 273.15 K and 373.15 K is 63.20 and 86.75 J/mol K, respectively. These parameters are summarized in Table S2. The entropies of gaseous water as a function of temperature are listed in Table S3. The isobaric heat capacities from Feistel and Wagner⁵ were converted to a smooth function using a cubic spline and integrated using Mathematica. The result of this integration is reported at various temperatures in Table S3.

Table S2: Relevant enthalpies and entropies for water/ice at phase transition temperatures.

Property	Value	Source
$\Delta H_{vap}(373.15K)$	40.66 kJ/mol	CRC Handbook ⁶
$\Delta H_{fus}(273.15K)$	6.01 kJ/mol	CRC Handbook ⁶
$\Delta S_{vap}(373.15K)$	109.0 J/mol K	$\Delta H_{vap}(373.15K)/373.15K$
$\Delta S_{fus}(273.15K)$	22.0 J/mol K	$\Delta H_{fus}(273.15K)/273.15K$
$S_{liquid}(373.15K)$	86.75 J/mol K	NIST/TRC Web Thermo Tables ⁷
$S_{liquid}(273.15K)$	63.20 J/mol K	NIST/TRC Web Thermo Tables ⁷

Table S3: Contributions to the empirical entropy of sublimation for ice Ih, in J/mol K.

Temperature (K)	S_{gas} (T)	$\int_T^{273.15K} \frac{C_{p,crystal}^{expt}(T)}{T} dT$	ΔS_{sub}^{empr} (T)
50	129.2	32.97	120.5
60	135.2	31.38	124.9
70	140.4	29.77	128.5
80	144.8	28.17	131.3
90	148.7	26.57	133.6
100	152.2	24.99	135.5
110	155.4	23.42	137.1
120	158.3	21.88	138.5
130	160.9	20.36	139.6
140	163.4	18.85	140.6
150	165.7	17.37	141.4
160	167.8	15.91	142.0
170	169.9	14.46	142.7
180	171.8	13.02	143.1
190	173.6	11.60	143.5
200	175.3	10.18	143.8
210	176.9	8.77	144.0
220	178.5	7.37	144.2
230	179.9	5.97	144.2
240	181.4	4.58	144.3
250	182.7	3.19	144.2
260	184.0	1.80	144.1
270	185.3	0.41	144.0
273.15	185.7	0.00	144.0
373.15	196.2	n/a	n/a

2.3 Empirical Enthalpy and Entropy Data for Acetic Acid

The empirical enthalpy and entropy of sublimation for orthorhombic acetic acid were determined according to,

$$\begin{aligned} \Delta H_{sub}^{empr}(T) = & H_{gas}(T) - H_{gas}(298.15K) + \Delta H_{vap}(298.15K) \\ & + H_{liquid}(298.15K) - H_{liquid}(289.6K) + \Delta H_{fus}(289.6K) \\ & + H_{solid}(289.6K) - H_{solid}(T) \end{aligned} \quad (7)$$

$$\begin{aligned} \Delta S_{sub}^{empr}(T) = & S_{gas}(T) - S_{gas}(391.7K) + \Delta S_{vap}(391.7K) \\ & + S_{liquid}(391.7K) - S_{liquid}(289.6K) + \Delta S_{fus}(289.6K) \\ & + S_{solid}(289.6K) - S_{solid}(T) \end{aligned} \quad (8)$$

The enthalpy of fusion at acetic acid's freezing point (289.6 K) used is 11.72 kJ/mol, as reported by Martin and Andon.⁸ The enthalpy of vaporization at 298.15 K used is 50.3 kJ/mol, as reported by Verevkin.⁹ The entropy of fusion was determined by dividing the enthalpy of fusion by its freezing point temperature, 289.6 K. The entropy of vaporization was determined by dividing the enthalpy of vaporization by acetic acid's boiling point temperature, 391.7 K. Since the enthalpy of vaporization is reported at 298.15 K, it was extrapolated to 391.7 K using the following equation:

$$\begin{aligned} \Delta H_{vap}(391.7K) = & \Delta H_{vap}(298.15K) + H_{gas}(391.7K) - H_{gas}(298.15K) \\ & - H_{liquid}(391.7K) + H_{liquid}(298.15K) \end{aligned} \quad (9)$$

The enthalpies and entropies of the solid, liquid, and gas were taken from the NIST/TRC Web Thermo Tables.⁷ The enthalpy for liquid acetic acid at 289.6 K, 298.15 K, and 391.7 K are 27.11, 28.14, and 40.74 kJ/mol, respectively. Tables S4, S5, and S6 summarize the parameters needed to evaluate Eq 7–9 and list the final sublimation enthalpies and entropies.

Table S4: Relevant enthalpies and entropies for acetic acid at phase transition temperatures.

Property	Value	Source
$\Delta H_{vap}(298.15K)$	50.3 kJ/mol	Verevkin ⁹
$\Delta H_{vap}(391.7K)$	44.3 kJ/mol	Eq 9
$\Delta H_{fus}(289.6K)$	11.72 kJ/mol	Martin & Andon ⁸
$H_{liquid}(391.7K)$	40.74 kJ/mol	NIST/TRC Web Thermo Tables ⁷
$H_{liquid}(298.15K)$	28.14 kJ/mol	NIST/TRC Web Thermo Tables ⁷
$H_{liquid}(289.6K)$	27.11 kJ/mol	NIST/TRC Web Thermo Tables ⁷
$\Delta S_{vap}(391.7K)$	113.2 J/mol K	$\Delta H_{vap}(391.7K)/391.7K$
$\Delta S_{fus}(289.6K)$	40.46 J/mol K	$\Delta H_{fus}(289.6K)/289.6K$
$S_{liquid}(391.7K)$	194.52 J/mol K	NIST/TRC Web Thermo Tables ⁷
$S_{liquid}(289.6K)$	154.41 J/mol K	NIST/TRC Web Thermo Tables ⁷

Table S5: Contributions to the empirical acetic acid enthalpy of sublimation, in kJ/mol.

Temperature (K)	$H_{gas}(T)$	$H_{solid}(T)$	$\Delta H_{sub}^{emp}(T)$
50	1.78	0.59	66.0
60	2.18	0.91	66.1
70	2.59	1.28	66.1
80	2.99	1.71	66.1
90	3.40	2.17	66.1
100	3.80	2.65	66.0
110	4.20	3.17	65.9
120	4.61	3.70	65.8
130	5.02	4.26	65.6
140	5.44	4.83	65.5
150	5.86	5.41	65.3
160	6.30	6.02	65.1
170	6.74	6.64	64.9
180	7.19	7.27	64.8
190	7.66	7.92	64.6
200	8.13	8.59	64.4
210	8.62	9.27	64.2
220	9.13	9.97	64.0
230	9.65	10.69	63.8
240	10.18	11.43	63.6
250	10.73	12.18	63.4
260	11.30	12.96	63.2
270	11.88	13.75	63.0
278	12.36	14.41	62.8
280	12.48	14.57	62.8
289.6	13.07	15.39	62.5
298.15	13.60	n/a	n/a
391.7	40.74	n/a	n/a

Table S6: Contributions to the empirical acetic acid entropy of sublimation, in J/mol K.

Temperature (K)	$S_{gas}(T)$	$S_{solid}(T)$	$\Delta S_{sub}^{emp}(T)$
50	203.6	17.767	191.0
60	210.9	23.63	192.4
70	217.1	29.43	192.8
80	222.5	35.06	192.6
90	227.3	40.46	192.0
100	231.5	45.6	191.0
110	235.4	50.49	190.0
120	238.9	55.14	188.9
130	242.2	59.57	187.8
140	245.3	63.8	186.6
150	248.2	67.85	185.5
160	251.0	71.74	184.4
170	253.7	75.49	183.3
180	256.3	79.12	182.3
190	258.8	82.63	181.3
200	261.3	86.05	180.4
210	263.7	89.39	179.4
220	266.0	92.65	178.5
230	268.3	95.84	177.6
240	270.6	98.97	176.8
250	272.8	102.06	175.9
260	275.1	105.1	175.1
270	277.3	108.11	174.3
278	279.0	110.49	173.6
280	279.4	111.09	173.4
289.6	281.5	113.95	172.7
391.7	302.6	n/a	n/a

2.4 Empirical Enthalpy Data for Imidazole

The empirically derived enthalpy of sublimation for imidazole was derived using the following equation:

$$\Delta H_{sub}^{empr}(T) = \Delta H_{sub}(298.15K) + H_{gas}(T) - H_{gas}(298.15K) + \int_T^{298.15K} C_{p,solid}(T)dT \quad (10)$$

The enthalpy of sublimation at 298.15 K is 83.1 kJ/mol according to Jiménez et al.¹⁰ The isobaric heat capacities from De Wit¹¹ were cubically splined and integrated with Mathematica. The gas phase enthalpy was determined using standard translational, rotational, and vibrational partition function expressions:

$$H_{gas}(T) = H_{gas,trans} + H_{gas,rot} + H_{gas,vib} \quad (11)$$

$$= \frac{5}{2}RT + \frac{3}{2}RT + N_A \sum_i \left(\frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{kBT}\right) - 1} \right) \quad (12)$$

Note that the electronic energy and zero vibrational point energy are not explicitly included in Eq 12, since they cancel in $H_{gas}(T) - H_{gas}(298.15K)$ in Eq 10. The gas phase vibrational frequencies reported by Billes et al.¹² were used to evaluate Eq 12: 3517, 3143, 3123, 3110, 1448, 1404, 1328, 1265, 1188, 1098, 1062, 1013, 988, 923, 898, 831, 758, 674, 663, 621, and 539 cm^{-1} . The gas and solid enthalpies are listed Table S7.

Table S7: Contributions to the empirical enthalpy of sublimation for imidazole, in kJ/mol.

Temperature (K)	$H_{gas}(T)$	$\int_{373.15K}^T \frac{C_{p,crystal}^{empr}(T)}{T} dT$	$\Delta H_{sub}^{empr}(T)$
90	3.00	12.86	86.3
100	3.33	12.44	86.2
110	3.67	12.00	86.1
120	4.01	11.54	86.0
130	4.36	11.07	85.9
140	4.72	10.58	85.7
150	5.09	10.07	85.6
160	5.47	9.55	85.5
170	5.86	9.01	85.3
180	6.27	8.45	85.2
190	6.69	7.87	85.0
200	7.14	7.27	84.8
210	7.60	6.65	84.7
220	8.08	6.00	84.5
230	8.59	5.33	84.4
240	9.12	4.63	84.2
250	9.67	3.90	84.0
260	10.24	3.15	83.8
270	10.84	2.37	83.7
280	11.47	1.56	83.5
283	11.66	1.31	83.4
290	12.11	0.73	83.3
298.15	12.66	0.00	83.1

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