Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ab Initio Thermodynamic Properties and Their Uncertainties for Crystalline α-Methanol.

Supporting Information

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TABLE S1
Crystal structures optimized using HMBI MP2/avtz and periodic PBE-D3(BJ) calculations.

		HMBI MP2/avtz			VASP PBE-D3(BJ)	
a		4.50442			4.41097	
b		4.82159			4.95289	
c		8.90009			8.97994	
	x	*y*	*Z*	*x*	*y*	*z*
O_1	0.45814	0.42943	0.17700	0.48559	0.45890	0.17384
H_1	0.63588	0.48601	0.23249	0.67861	0.49031	0.23203
C_1	0.52062	0.16906	0.10685	0.50218	0.19752	0.10543
H_2	0.34250	0.12629	0.02731	0.70704	0.17928	0.03618
H_3	0.53069	0.00117	0.18903	0.30362	0.17361	0.03305
H_4	0.73024	0.17711	0.04519	0.50193	0.03451	0.18873

FIGURE S1. Overlays of optimized and experimental crystal structures: left – HMBI MP2/avtz; right – periodic PBE-D3(BJ).

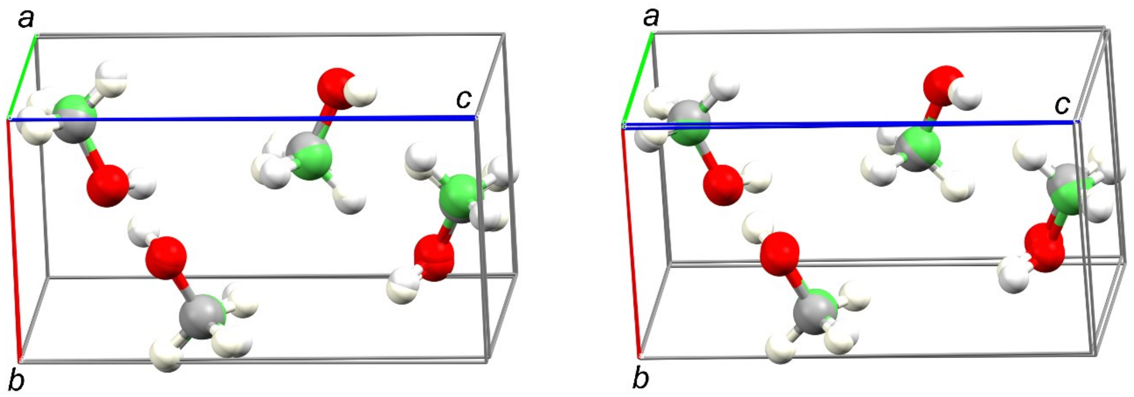

TABLE S2

Comparison of interaction energies (kcal·mol^{-1}) for the methanol dimer from the S66x8 data set calculated at various levels of theory.

R	CCSD(T)/cbs	MP2/avtz	MP2/avqz	MP2/cbs	PBE-D3(BJ)/PAW	PBE-D3(BJ)/avqz
0.90	-5.280	-5.048	-5.301	-5.565	-5.865	-5.62
0.95	-5.690	-5.467	-5.680	-5.929	-6.181	-5.97
1.00	-5.750	-5.536	-5.715	-5.940	-6.165	-5.99
1.05	-5.580	-5.391	-5.537	-5.735	-5.947	-5.79
1.10	-5.280	-5.120	-5.238	-5.406	-5.612	-5.48
1.25	-4.140	-4.046	-4.105	-4.200	-4.394	-4.30
1.50	-2.520	-2.496	-2.514	-2.545	-2.689	-2.63
2.00	-1.010	-1.010	-1.016	-1.020	-1.038	-1.02

TABLE S3
Calculated and literature experimental fundamental Γ-point vibrational frequencies (cm^{-1}) for α-methanol. Calculated frequencies correspond to the electronic-energy based optimized unit cells. Comparison of the lattice modes should be considered as rather tentative.

Experiment		Calculation		
Ref. [a]	Ref. [b]	MP2/avdz*	MP2/avtz*	PBE-D3(BJ)
Intramolecular modes				
685	677	709.4, 717.4	729.8, 737.6	809.9, 810.1
790	764	823.0, 847.5	836.0, 859.1	970.8, 980.6
1029	1020	1029.4	1044.7	1016.0
1029	1025	1036.1	1048.1	1023.5
1046	1032	1045.2, 1050.5	1055.5, 1057.6	1027.7, 1041.4
1142	1142	1123.1, 1124.7	1139.0, 1140.2	1104.3, 1107.2
1162	1158	1154.7, 1156.7	1174.1, 1175.0	1138.5, 1138.8
1256	n/a	1170.5, 1171.9, 1175.0, 1175.5	1185.3, 1185.6, 1189.0, 1189.6	1140.1, 1141.9, 1142.2, 1147.6
1345	1334	1451.2, 1456.4, 1464.6, 1465.0	1468.2, 1473.0, 1475.1, 1491.4	1420.3, 1428.0, 1431.9, 1438.1
1426	1430	1467.2, 1480.0, 1484.7, 1488.3	1492.0, 1505.1, 1512.8, 1513.0	1441.5, 1446.0, 1452.7, 1455.6
1445	1456	1495.3, 1496.5	1515.7, 1523.5	1459.1, 1466.0
1458	1472	1496.8, 1501.4	1524.7, 1525.0	1472.9, 1476.9
1470	1472	1511.7, 1513.8	1533.5, 1542.9	1479.4, 1488.1
1514	1512	1539.8, 1559.8	1554.9, 1577.8	1549.8, 1558.4
2829	2832	3042.9, 3044.7, 3046.1, 3046.8	3037.8, 3039.3, 3041.3, 3042.1	2827.0, 2827.4, 2937.6, 2939.5
2912	2907	3133.4, 3134.1	3123.6, 3124.8	2945.1, 2949.7
2912	2929	3137.1, 3140.1	3127.3, 3129.4	3012.0, 3012.2
2982	2985	3165.7, 3166.1	3151.6, 3153.2	3016.0, 3017.8
2955	2958	3168.0, 3169.4	3153.9, 3156.6	3049.3, 3049.4
3187	3189	3520.8, 3534.1	3495.1, 3508.6	3051.5, 3051.6
3284	3291	3570.3, 3585.9	3543.8, 3559.3	3063.5, 3117.0

[a] Falk, M.; Whalley, E., Infrared Spectra of Methanol and Deuterated Methanols in Gas, Liquid, and Solid Phases. *J. Chem. Phys.* **1961,** *34*, 1554-1568.

[b] Galvez, O.; Mate, B.; Martin-Llorente, B.; Herrero, V. J.; Escribano, R., Phases of Solid Methanol. *J. Phys. Chem. A* **2009,** *113*, 3321-3329.

Experiment	Calculation		
Ref. [c]	MP2/avdz*	MP2/avtz*	PBE-D3(BJ)
Lattice modes			
356	364.7	396.2	421.4
328	362.7	393.8	413.2
278.5	226.3	228.2	212.0
	213.6	213.1	207.6
	190.1	200.3	206.1
231	180.1	192.8	202.7
216	164.7	165.0	173.7
180	158.3	156.4	161.9
168	139.8	143.7	141.3
147	134.1	141.8	137.5
133	129.3	129.6	135.5
120	124.2	125.9	133.7
	119.6	123.8	128.9
101	107.1	110.3	117.9
91	97.1	104.7	109.6
85.5	86.6	87.2	106.1
81	80.0	83.1	94.0
	64.7	69.5	77.2
73.5	60.9	68.5	74.4
64	53.0	66.7	73.6
54.5	16.8	23.0	13.4

[c] Anderson, A.; Andrews, B.; Meiering, E. M.; Torrie, B. H., Raman and Far-Infrared Study of the Lattice-Vibrations of Methanol. *J. Raman Spectrosc.* **1988,** *19*, 85-89.

TABLE S4

Literature experimental and calculated fundamental Γ-point vibrational frequencies (cm^{-1}) for the lattice modes of α-methanol at 20 K. Calculated values obtained using quasi-harmonic approximation and the Grüneisen parameters.

Experiment	Calculation		
Ref. [a]	MP2/avdz*	MP2/avtz*	PBE-D3(BJ)
	Lattice modes		
356	349.1	379.2	396.9
328	347.4	377.4	389.6
278.5	203.3	207.1	201.0
	191.4	194.1	190.0
	180.9	186.2	189.7
231	170.4	177.3	182.9
216	155.2	155.2	161.3
180	151.4	146.9	160.8
168	129.8	132.8	144.3
147	122.9	130.6	136.2
133	118.9	118.5	134.8
120	114.7	116.6	127.8
	109.6	116.5	127.5
101	99.0	108.0	105.9
91	85.2	87.2	94.2
85.5	77.7	81.6	93.4
81	74.9	80.6	90.2
	54.4	65.6	73.6
73.5	52.0	59.4	62.2
64	41.7	55.0	53.0
54.5	15.2	21.1	37.9

[a] Anderson, A.; Andrews, B.; Meiering, E. M.; Torrie, B. H., Raman and Far-Infrared Study of the Lattice-Vibrations of Methanol. *J. Raman Spectrosc.* **1988,** *19*, 85-89.

FIGURE S2. Pressure dependence of molar volume of α-methanol calculated for selected temperatures at the CCSD(T)/cbs level of theory (solid lines from the quasi-anisotropic (•) model, dashed lines from the isotropic (*) model).

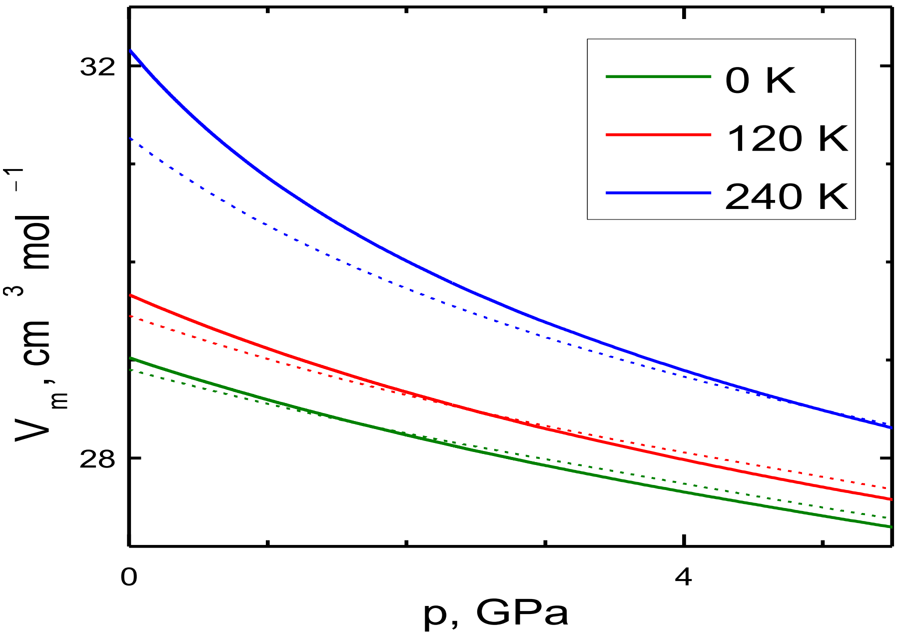

FIGURE S3. Illustration of the effect of the fitting form and the quality of the fit of the total Helmholtz energy as a function of unit cell volume of α-methanol. Molar volumes correspond to the isotropic MP2/avdz* level of theory.

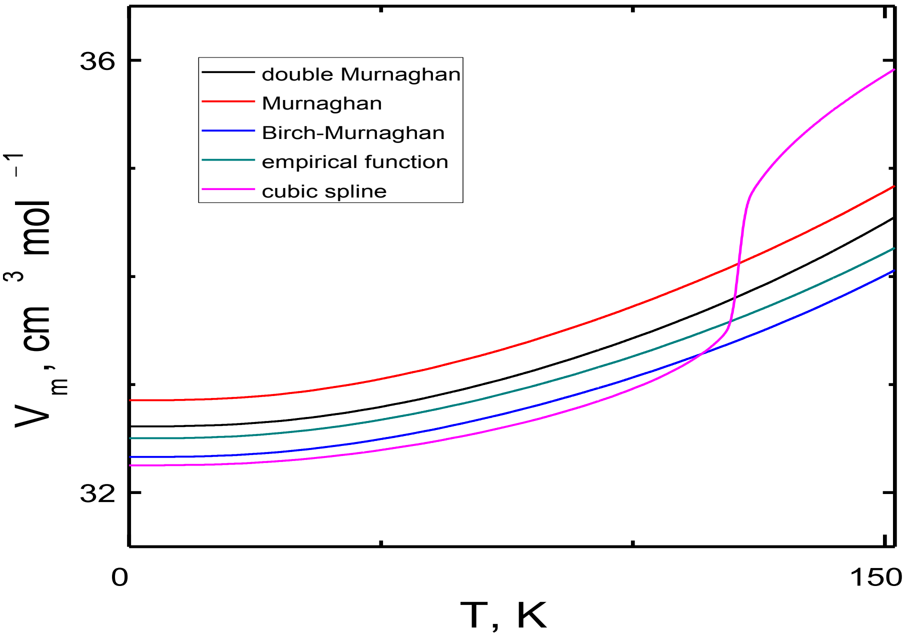

TABLE S5

Functional forms and corresponding RMSE (in kJ·mol^{-1}) of given Helmholtz energy fits.

Function	Functional form	RMSE
Double Murnaghan eq.[a]	-	0.043
Murnaghan eq.	$A = A_0 + \frac{B_0 V}{B_0^{'}}\left[\frac{\left({}^{V_0}\!/\!{}_{V}\right)^{B_0^{'}}}{B_0^{'} - 1}\right] - \frac{B_0 V_0}{B_0^{'} - 1}$	0.109
Birch-Murnaghan eq.	$A = \frac{k_0}{2}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left[k_1 - k_2\left(\frac{V_0}{V}\right)^{2/3} - k_3\left(\frac{V_0}{V}\right)^{4/3}\right]$	0.123
Empirical eq.	$A = p_1 + p_2 V + p_3 V^2 + p_4 V^{-1} + p_5 V^{-2} + p_6 V^{-3}$	0.077
Cubic Spline	$A = c_{i,0} + c_{i,1} V + c_{i,2} V^2 + c_{i,3} V^3$	0.000

[a] Uses two separate Murnaghan equations for the compression and expansion branches of Helmholtz energy profiles. Given functional form grants that both functions are smoothly joined in the minimum point.

FIGURE S4. Pressure dependence of isobaric heat capacities of α-methanol calculated for selected temperatures at the quasi-anisotropic CCSD(T)/cbs• level of theory.