Electronic Supplementary Information

Co-crystals, salts and ionic co-crystals of ethanol and ammonia

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Supplementary Figures

Figure S1

Stack-plot of neutron powder diffraction data collected from ethanol hemi-ammoniate. The uppermost profile reports the long measurement at 175 K that was used for the structure refinement. Subsequent profiles moving down the stack are at 170 K and then in 10 K increments to 70 K. The bottom profile (70 K) appears noisier due to a shorter counting time.

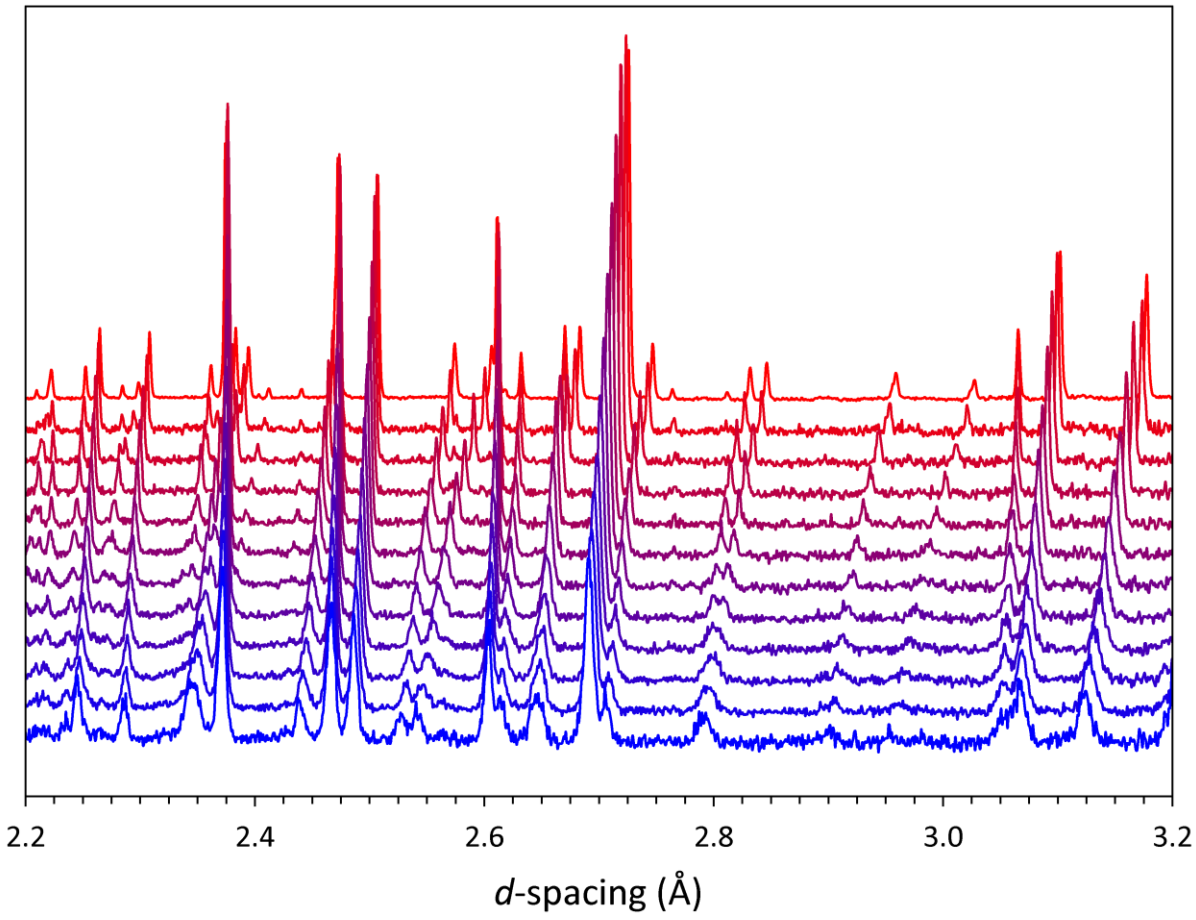
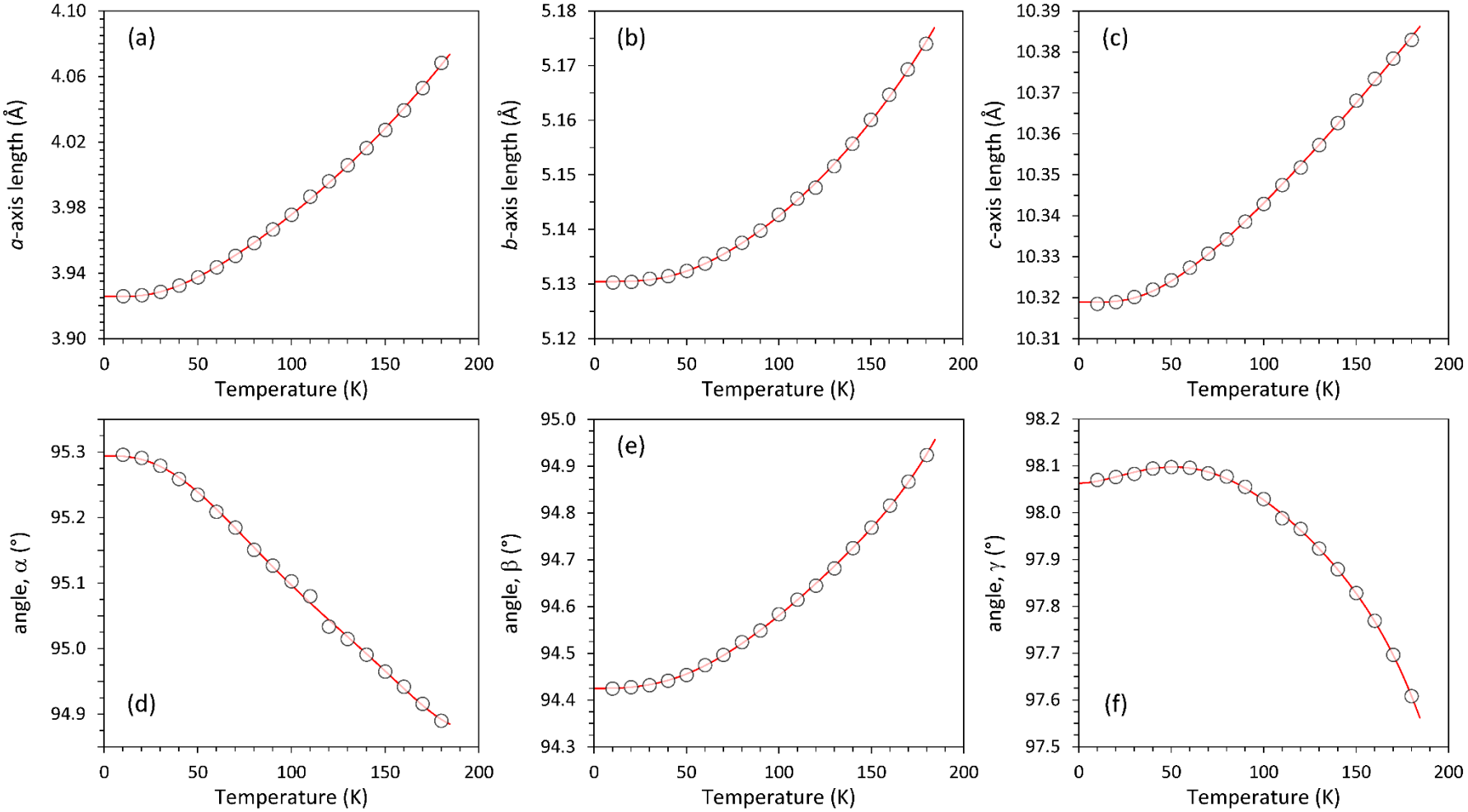


Figure S2

Unit-cell parameters of ethanol mono-ammoniate between 10 and 180 K: (a) *a*-axis; (b) *b*-axis; (c) *c*-axis; (d) angle α; (e) angle β; (f) angle γ; (g) unit-cell volume (overleaf). Open circles represent the observations and the solid lines are Debye model or polynomial fits (see main text and Table S3)



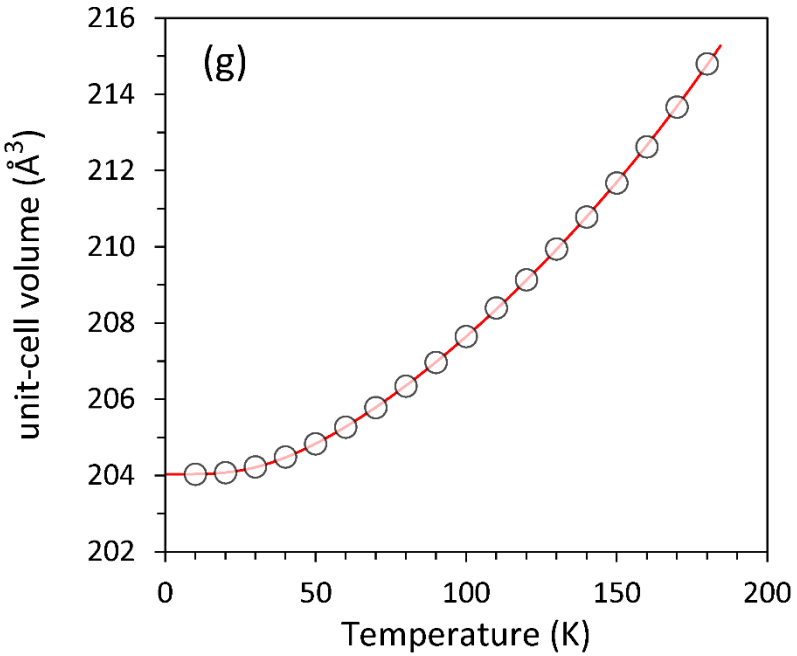
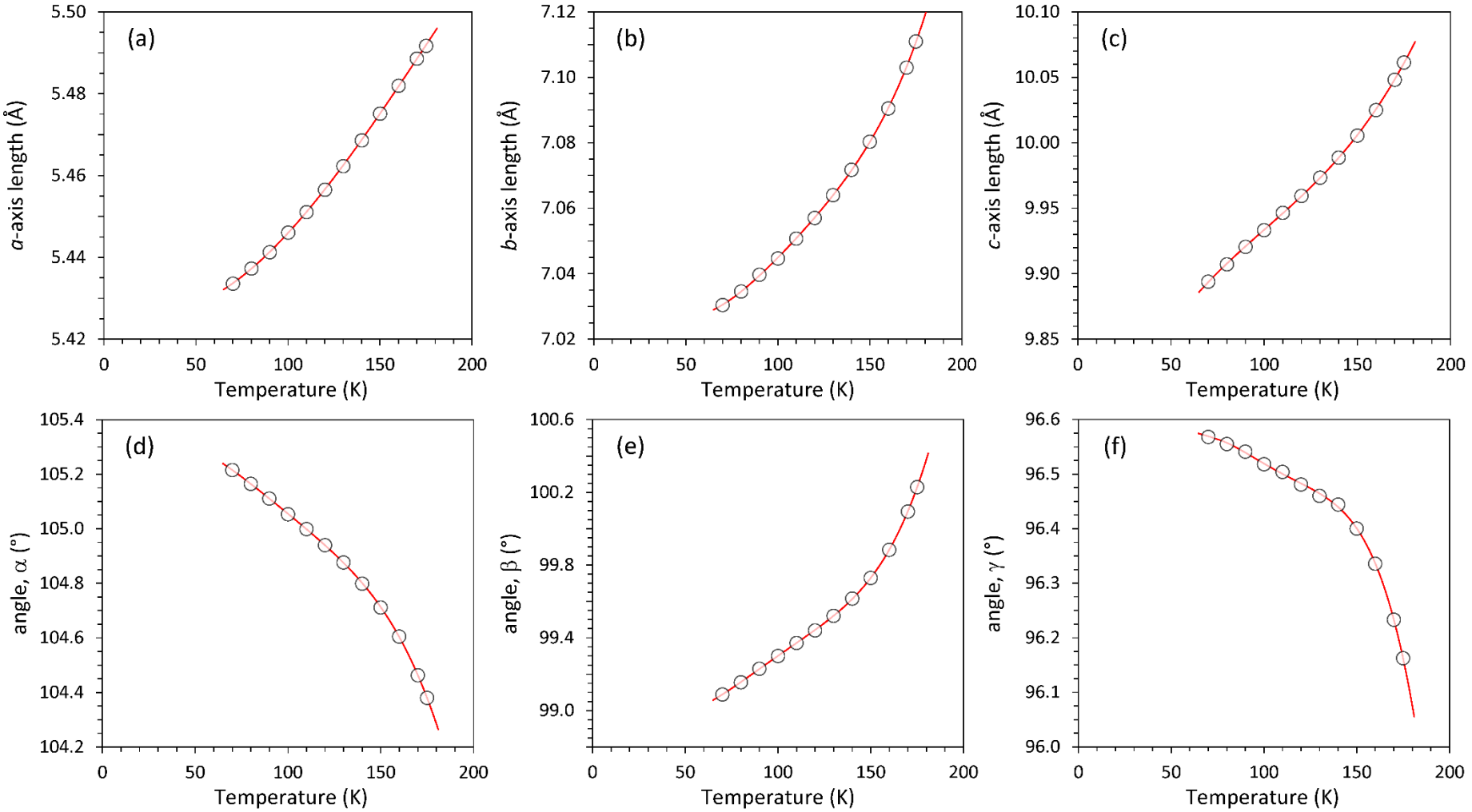

(g)
unit-cell volume (Å^3)
216
214
212
210
208
206
204
202
0
50
100
150
200
Temperature (K)

Figure S3

Unit-cell parameters of ethanol hemi-ammoniate between 70 and 175 K: (a) *a*-axis; (b) *b*-axis; (c) *c*-axis; (d) angle α; (e) angle β; (f) angle γ; (g) unit-cell volume (overleaf). Open circles represent the observations and the solid lines are polynomial fits (see main text)



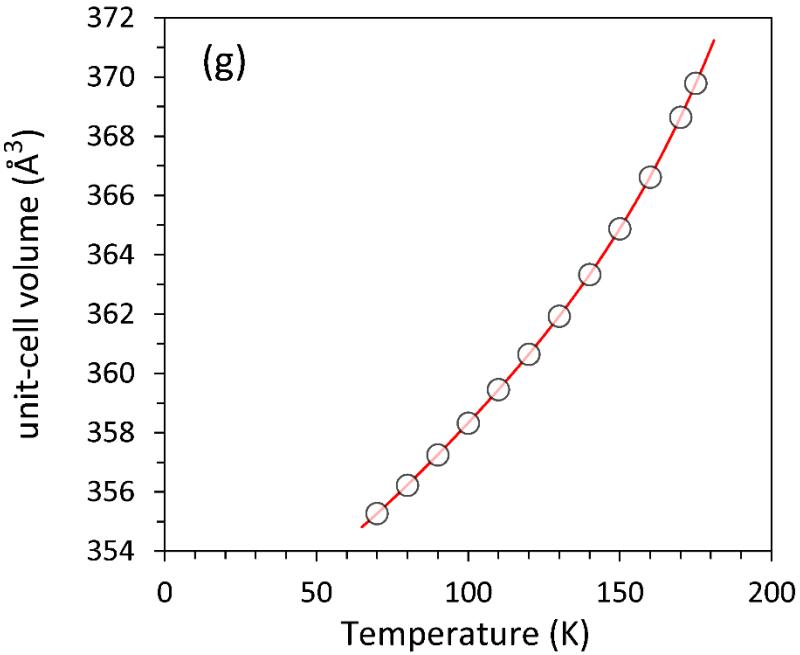
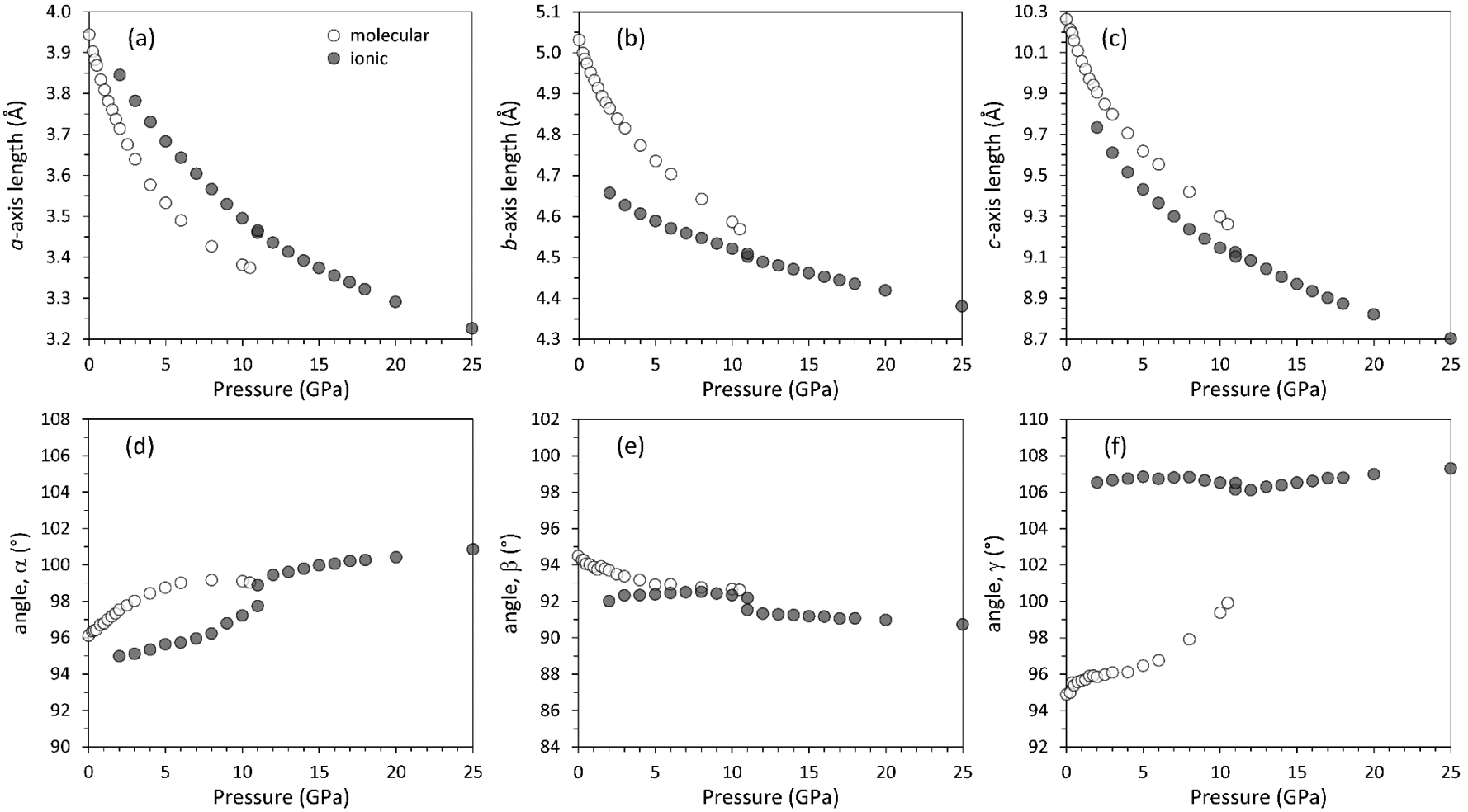

(g)
unit-cell volume (Å^3)
372
370
368
366
364
362
360
358
356
354
0
50
100
150
200
Temperature (K)

Figure S4

Unit-cell parameters of ethanol mono-ammoniate obtained from DFT calculations over the range of pressures 0 – 25 GPa: (a) *a*-axis; (b) *b*-axis; (c) *c*-axis; (d) angle α; (e) angle β; (f) angle γ; (g) unit-cell volume (overleaf). Open circles correspond with the molecular co-crystal and filled circles correspond to the ionic crystal.



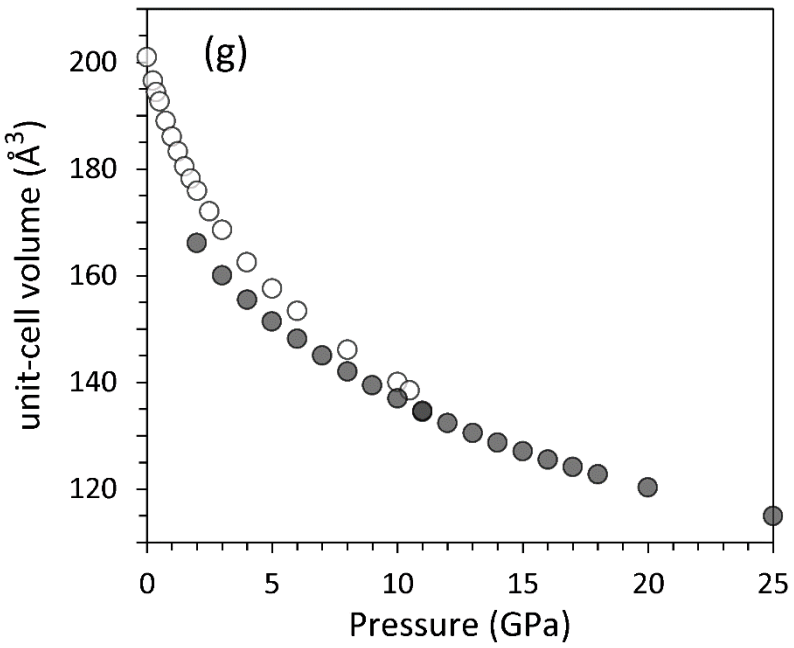
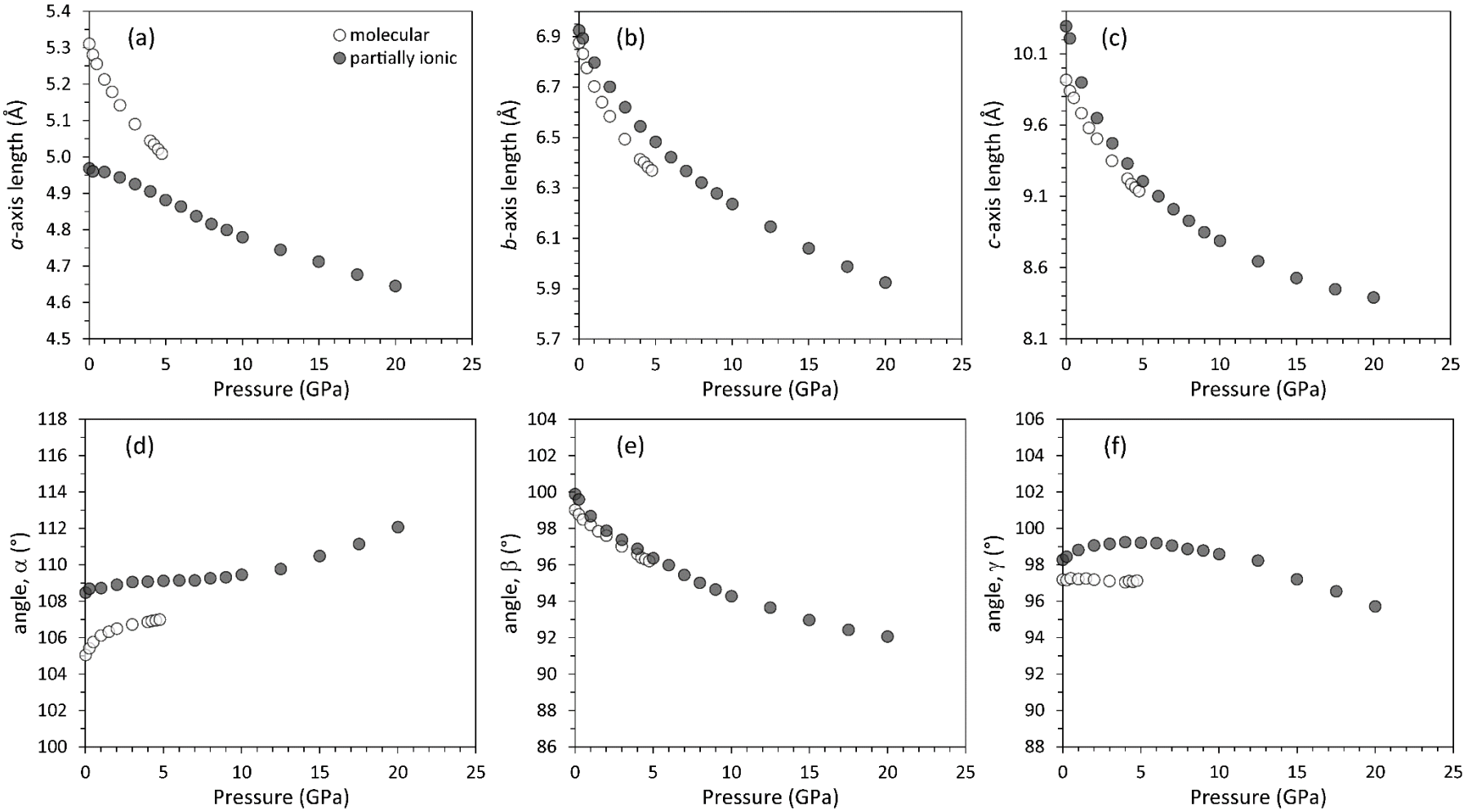

(g)
unit-cell volume (Å^3)
200
180
160
140
120
0
5
10
15
20
25
Pressure (GPa)

Figure S5

Unit-cell parameters of ethanol hemi-ammoniate obtained from DFT calculations over the range of pressures 0 – 20 GPa: (a) *a*-axis; (b) *b*-axis; (c) *c*-axis; (d) angle α; (e) angle β; (f) angle γ; (g) unit-cell volume (overleaf). Open circles correspond with the molecular co-crystal and filled circles correspond to the ionic co-crystal.



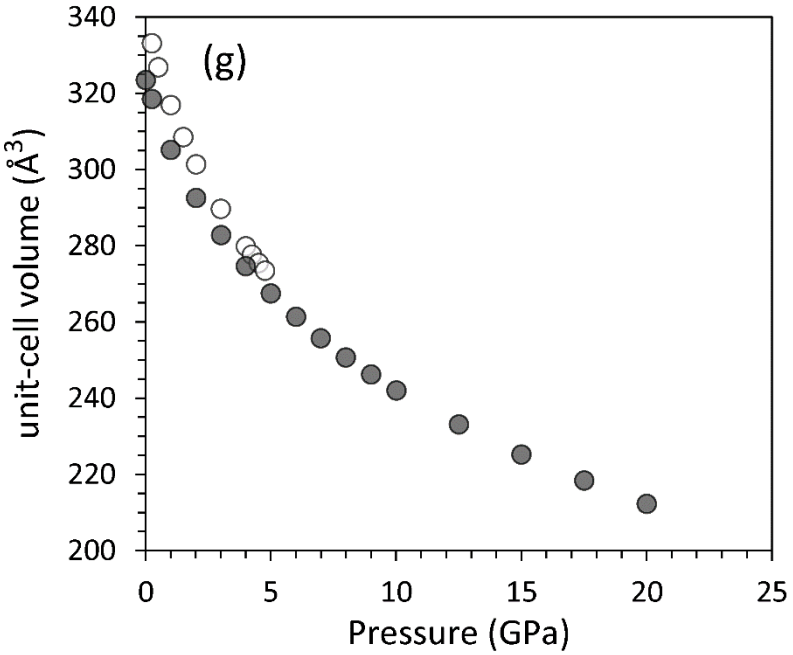

(g)
unit-cell volume (Å^3)
340
320
300
280
260
240
220
200
0
5
10
15
20
25
Pressure (GPa)

Table S1

Refined unit-cell parameters of ethanol mono-ammoniate. These data are plotted in Fig. S2.

T (K)	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	V (Å^3)
180	4.06831(2)	5.17400(2)	10.38296(4)	94.8905(4)	94.9238(4)	97.6082(3)	214.796(1)
170	4.05297(3)	5.16932(3)	10.37842(6)	94.916(1)	94.867(1)	97.696(1)	213.664(2)
160	4.03938(3)	5.16469(3)	10.37348(6)	94.942(1)	94.816(1)	97.769(1)	212.626(2)
150	4.02744(3)	5.16011(3)	10.36812(7)	94.965(1)	94.769(1)	97.828(1)	211.676(2)
140	4.01635(4)	5.15569(4)	10.36266(9)	94.991(1)	94.725(1)	97.879(1)	210.780(2)
130	4.00592(5)	5.15160(5)	10.35727(11)	95.015(1)	94.682(1)	97.923(1)	209.938(3)
120	3.99609(6)	5.14768(6)	10.35179(13)	95.034(1)	94.645(1)	97.965(1)	209.137(3)
110	3.98663(7)	5.14565(8)	10.34752(14)	95.080(1)	94.615(1)	97.988(1)	208.396(4)
100	3.97561(6)	5.14271(6)	10.34291(13)	95.103(1)	94.584(1)	98.029(1)	207.647(4)
90	3.96668(6)	5.13982(6)	10.33861(13)	95.127(1)	94.549(1)	98.055(1)	206.966(4)
80	3.95831(7)	5.13759(7)	10.33426(14)	95.151(1)	94.524(1)	98.077(2)	206.340(4)
70	3.95055(7)	5.13551(7)	10.33077(15)	95.185(1)	94.497(1)	98.084(2)	205.776(4)
60	3.94358(7)	5.13377(7)	10.32737(15)	95.209(1)	94.475(1)	98.096(2)	205.267(4)
50	3.93749(7)	5.13245(7)	10.32426(16)	95.235(1)	94.454(2)	98.097(2)	204.833(4)
40	3.93245(7)	5.13146(7)	10.32203(16)	95.259(1)	94.442(1)	98.094(2)	204.484(4)
30	3.92857(7)	5.13100(7)	10.32021(17)	95.279(1)	94.432(1)	98.083(2)	204.228(4)
20	3.92649(7)	5.13043(7)	10.31895(16)	95.291(1)	94.428(1)	98.076(2)	204.074(4)
10	3.92592(5)	5.13030(5)	10.31853(11)	95.296(1)	94.425(1)	98.070(1)	204.033(3)

Table S2

Refined unit-cell parameters of ethanol hemi-ammoniate. These data are plotted in Fig. S3.

T (K)	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	V (Å^3)
175	5.49172(1)	7.11096(2)	10.06131(2)	104.3802(2)	100.2283(2)	96.1623(2)	369.793(1)
170	5.48859(3)	7.10297(5)	10.04815(6)	104.4630(5)	100.0948(4)	96.2331(6)	368.644(3)
160	5.48197(3)	7.09051(5)	10.02501(6)	104.6053(5)	99.8834(5)	96.3358(6)	366.628(3)
150	5.47517(4)	7.08034(6)	10.00558(8)	104.712(1)	99.729(1)	96.400(1)	364.882(3)
140	5.46864(5)	7.07179(9)	9.98880(11)	104.799(1)	99.616(1)	96.444(1)	363.342(5)
130	5.46235(5)	7.06404(8)	9.97347(10)	104.877(1)	99.521(1)	96.460(1)	361.933(4)
120	5.45655(6)	7.05704(10)	9.95943(13)	104.940(1)	99.441(1)	96.481(1)	360.647(5)
110	5.45111(6)	7.05076(10)	9.94649(14)	104.999(1)	99.372(1)	96.504(1)	359.457(6)
100	5.44610(7)	7.04468(11)	9.93329(15)	105.053(1)	99.300(1)	96.518(1)	358.320(6)
90	5.44128(7)	7.03970(12)	9.92058(17)	105.111(1)	99.230(1)	96.541(2)	357.250(7)
80	5.43729(8)	7.03461(13)	9.90727(18)	105.165(1)	99.156(1)	96.555(2)	356.230(7)
70	5.43361(13)	7.03045(20)	9.89395(26)	105.215(2)	99.088(2)	96.568(3)	355.28(1)

Table S3

Parameters obtained from fitting a 2nd order Debye model to the unit-cell edges (*a*, *b*, *c*) and the unit-cell volume of ethanol mono-ammoniate, and fitting of modified polynomials to the inter-axial angles (α, β, γ). The polynomial functions are of the form, $a(T) = a_0 + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5 + a_6T^6$. The results are plotted as solid lines in Figure S2.

Debye	*a*-axis	*b*-axis	*c*-axis	Volume
V_0 (Å, Å$_3$)	3.9257(16)	5.1305(6)	10.3189(8)	204.034(13)
θ_D (K)	149(11)	236(21)	186(13)	165(4)
K_0/γ (GPa)	29(1)	48(5)	6.7(5)	17.2(3)
K_0'	7.8(8)	37(6)	9.9(5)	14.9(6)
Polynomial	α	β	γ	
a_0	95.294(3)	94.425(1)	98.063(3)	
a_2	0	0	$5.3(5)\times10^{-5}$	
a_3	$-9.3(8)\times10^{-7}$	$3.7(1)\times10^{-7}$	$-1.1(1)\times10^{-6}$	
a_4	$1.3(2)\times10^{-9}$	$-2.9(1)\times10^{-9}$	$6.4(8)\times10^{-9}$	
a_5	$-6.6(12)\times10^{-11}$	$7.1(5)\times10^{-12}$	$-1.5(2)\times10^{-11}$	
a_6	$1.2(3)\times10^{-14}$	0	0	

Table S4

Refined unit-cell parameters of deutero-ammonia. These data are plotted in the main text, Figure 12.

T (K)	*a* (Å)
180	5.13559(2)
170	5.12765(3)
160	5.11984(3)
150	5.11272(3)
140	5.10591(3)
130	5.0997(2)
120	5.0936(2)
110	5.0881(2)
100	5.0829(2)
90	5.0781(2)
80	5.0739(2)
70	5.0699(2)
60	5.0667(2)
50	5.0639(2)
40	5.0617(2)
30	5.0603(2)
20	5.0596(2)
10	5.0593(2)

Table S5

Comparison of the experimental low-temperature unit-cell parameters of ethanol mono- and hemi-ammoniate with those found at zero pressure and temperature by DFT calculation.

	Ethanol mono-ammoniate			Ethanol hemi-ammoniate		
	Expt. 10 K	DFT 0 K	Δ (%)	Expt. 70 K	DFT 0 K	Δ (%)
a (Å)	3.92592(5)	3.944321	0.469	5.4336(1)	5.310610	−2.264
b (Å)	5.13030(5)	5.031089	−1.934	7.0305(2)	6.875528	−2.204
c (Å)	10.3185(1)	10.26296	−0.539	9.8940(3)	9.918167	0.248
α (°)	95.296(1)	96.10376	0.848	105.215(2)	105.04375	−0.163
β (°)	94.425(1)	94.49019	0.069	99.088(2)	99.02780	−0.061
γ (°)	98.070(1)	94.87766	−3.255	96.568(3)	97.17857	0.632
V (Å^3)	204.033(3)	200.98713	−1.493	355.28(1)	340.14873	−4.258
b/*a*	1.30678(2)	1.27553	−2.391	1.29388(5)	1.29468	0.061
c/*a*	2.62831(5)	2.60196	−1.002	1.82088(6)	1.86761	2.566

Table S6

Parameters obtained from fitting of a 4th order logarithmic equation of state to the $E(V)$ curves of ethanol mono- and hemi-ammoniates in both their molecular and ionic forms. See main text for details of the fitted equations and Figure 14 for a plot of the curves. Since the ionic mono-ammoniate could not be relaxed below 2 GPa, the shape of the $E(V)$ curve around V_0 is not constrained and consequently the uncertainty in the fit parameters is poor. Furthermore, the value of K_0'' had to be fixed and a choice was made to use the same value found in the molecular phase.

	Ethanol mono-ammoniate		Ethanol hemi-ammoniate	
	Molecular $C_2H_5OH{\cdot}NH_3$	Ionic $C_2H_5O^-{\cdot}NH_4^+$	Molecular $2(C_2H_5OH){\cdot}NH_3$	Partially ionic $C_2H_5OH{\cdot}\ C_2H_5O^-{\cdot}NH_4^+$
V_0 (Å^3)	197.98(16)	181.8(14)	334.90(22)	319.86(10)
K_0 (GPa)	10.8(1)	15.4(12)	11.9(2)	14.00(6)
K_0'	5.9(4)	6.1(1)	7.6(2)	8.8(1)
K_0'' (GPa^{-1})	−1.1(7)	−1.1 *	−3.6(7)	−4.3(2)
E_0 (eV)	−2328.5126(6)	−2328.24(1)	−4016.5736(7)	−4016.6033(7)

*Fixed at same value as in molecular EMA.