Supplemental Information

Liquid structure of primary ammonium nitrate ionic liquids studied by high-energy X-ray diffraction experiments and MD simulations

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Table S1. Lennard-Jones parameters and partial atomic point charges for $[C_nAm^+]$ (n = 2, 3, and 4) and nitrate ions.

ammonium				nitrate			
atoms	σ / Å	ε / kcal mol^{-1}	q / e	atoms	σ / Å	ε / kcal mol^{-1}	q / e
CT	3.50	0.066	– 0.18	NN	3.25	0.170	0.905
CS	3.50	0.066	– 0.12	ON	2.96	0.210	– 0.635
CE	3.50	0.066	– 0.05				
C2	3.50	0.066	0.01				
C1	3.50	0.066	0.04				
N3	3.25	0.170	– 0.36				
HC	2.50	0.030	0.06				
H1	2.50	0.030	0.13				
HN	2.50	0.030	0.31				

Table S2. The experimental density and simulated data of $[C_nAm^+][NO_3^-]$ (n = 2, 3, and 4).

n	$\rho_{obs.}$ / g cm^{-3}	ρ_{MD} / g cm^{-3}	$\Delta\rho$ / %
2	1.2109(1)	1.224(5)	1.1
3	1.1620(1)	1.158(5)	0.3
4	1.1089(1)	1.104(4)	0.4

Figure S1.

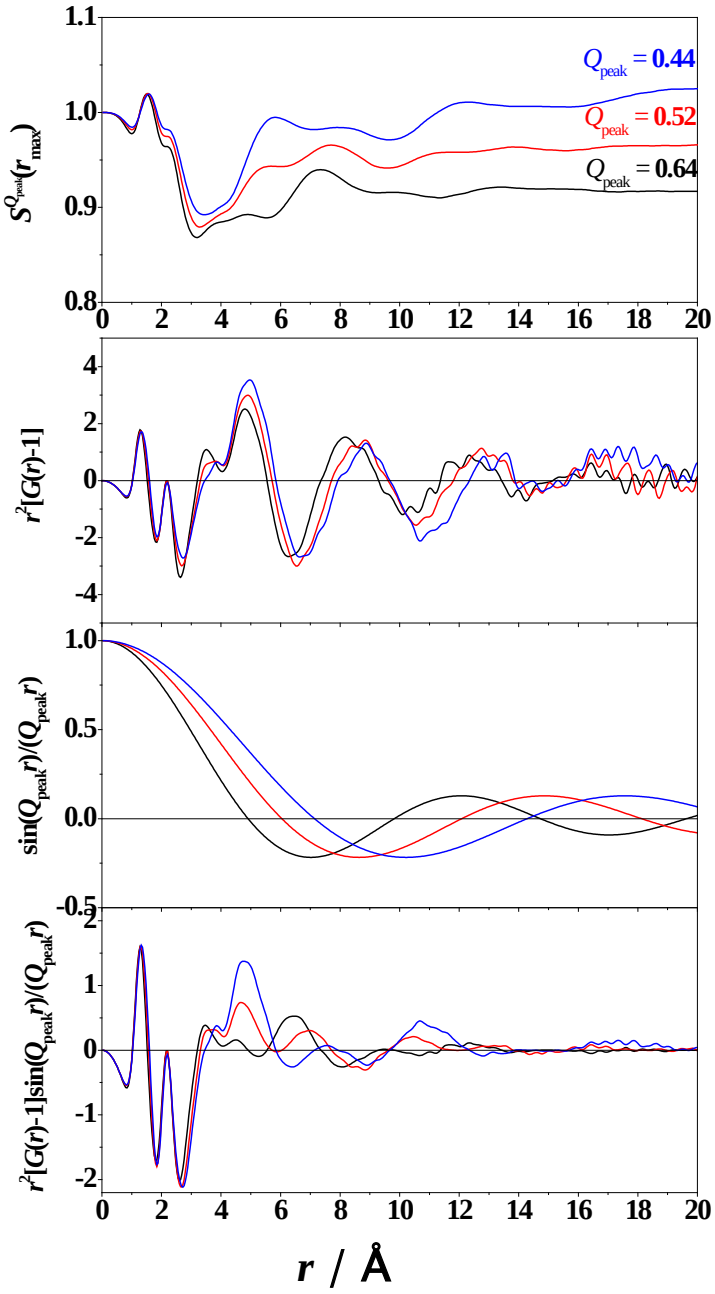

Figure S1. $S^{Q_{peak}}(r_{max})$, $r^2[G(r)-1]$, $\frac{\sin(Q_{peak}r)}{Q_{peak}r}$ and $r^2[G(r)-1]\frac{\sin(Q_{peak}r)}{Q_{peak}r}$ with Q_{peak} = 0.64 Å^{-1} for $[C_2Am^+][NO_3^-]$ (black), 0.52 Å^{-1} for $[C_3Am^+][NO_3^-]$ (red) and 0.44 Å^{-1} for $[C_4Am^+][NO_3^-]$ (blue) obtained by the HEXRD experiments.

Figure S2.

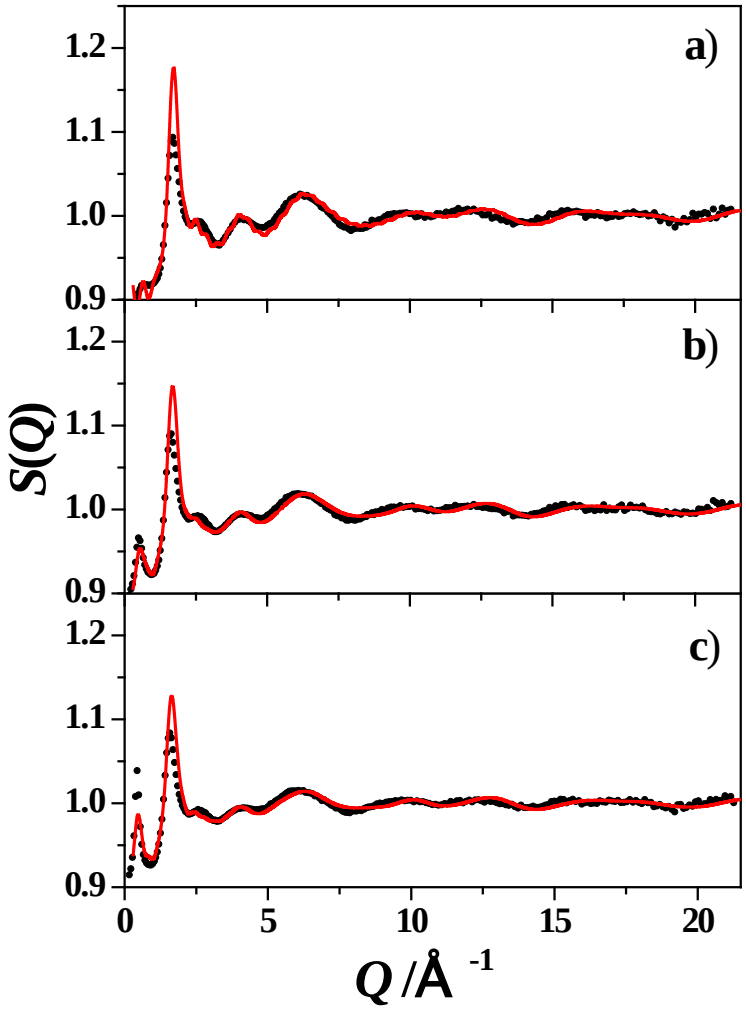

Figure S2. X-ray structure factors $S(Q)$ obtained from the HEXRD experiments (black dots) and MD simulations (a red line) for protic ionic liquids: (a) $[C_2Am^+][NO_3^-]$, (b) $[C_3Am^+][NO_3^-]$, and (c) $[C_4Am^+][NO_3^-]$.

Figure S3.

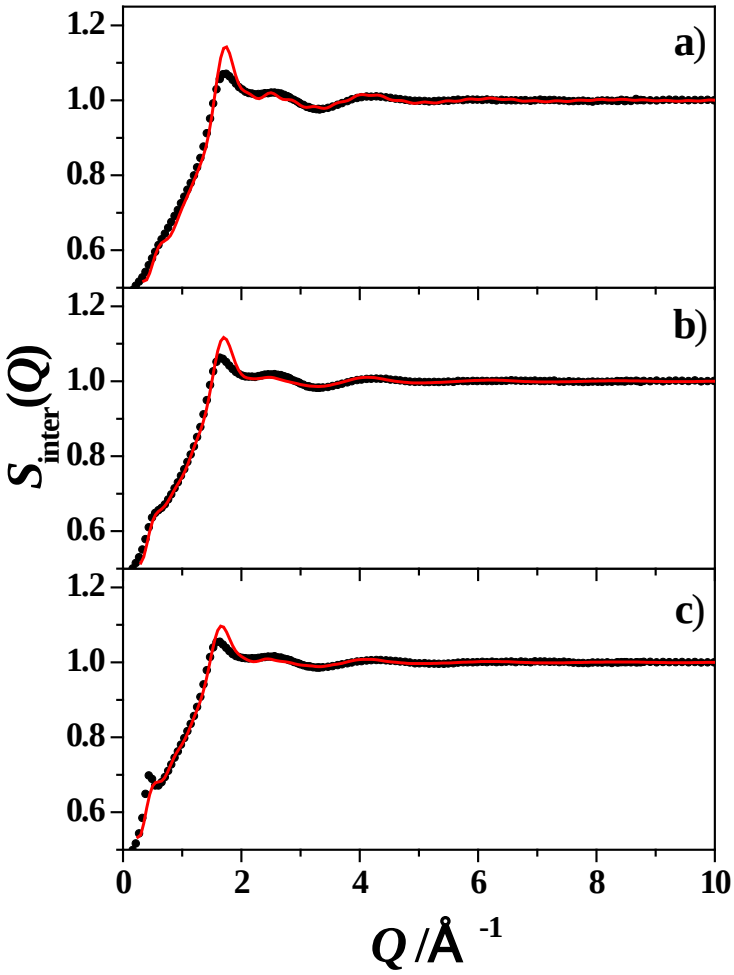

Figure S3. Inter-molecular structure factors $S_{inter}(Q)$ extracted from the HEXRD experiments (black dots) and derived from MD simulations (a red line) for (a) $[C_2Am^+][NO_3^-]$, (b) $[C_3Am^+][NO_3^-]$, and (c) $[C_4Am^+][NO_3^-]$.

Figure S4.

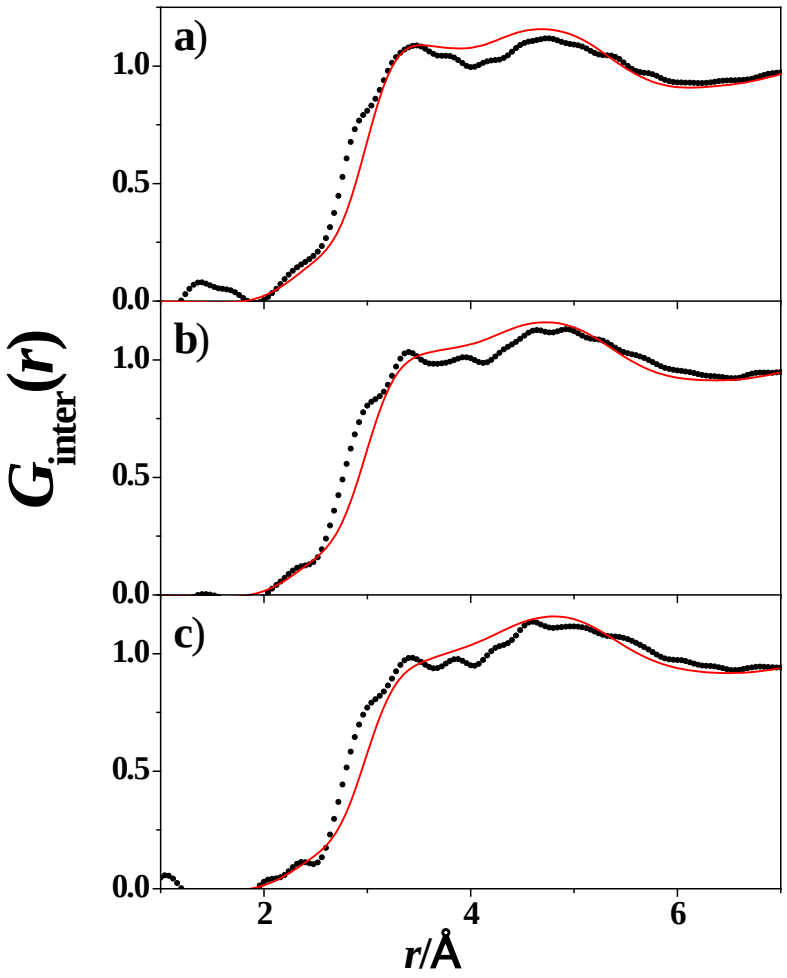

Figure S4. Inter-molecular X-ray radial distribution functions $G_{inter}(r)$ extracted by the HEXRD experiments (black dots) and derived from MD simulations (a red line) for (a) $[C_2Am^+][NO_3^-]$, (b) $[C_3Am^+][NO_3^-]$, and (c) $[C_4Am^+][NO_3^-]$.

Figure S5.

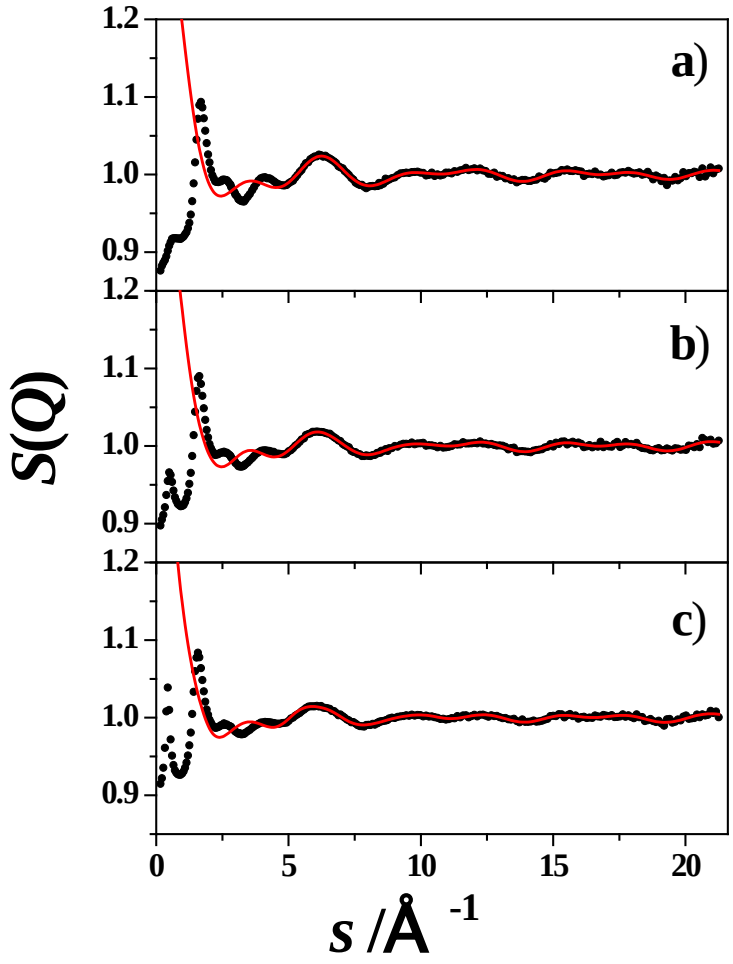

Figure S5. X-ray structure factors $S(Q)$ obtained by the HEXRD experiments (black dots) and the intra-molecular structure factors estimated based on the molecular geometries found in crystal structure also shown as a red line. (a) $[C_2Am^+][NO_3^-]$, (b) $[C_3Am^+][NO_3^-]$, and (c) $[C_4Am^+][NO_3^-]$.

Figure S6.

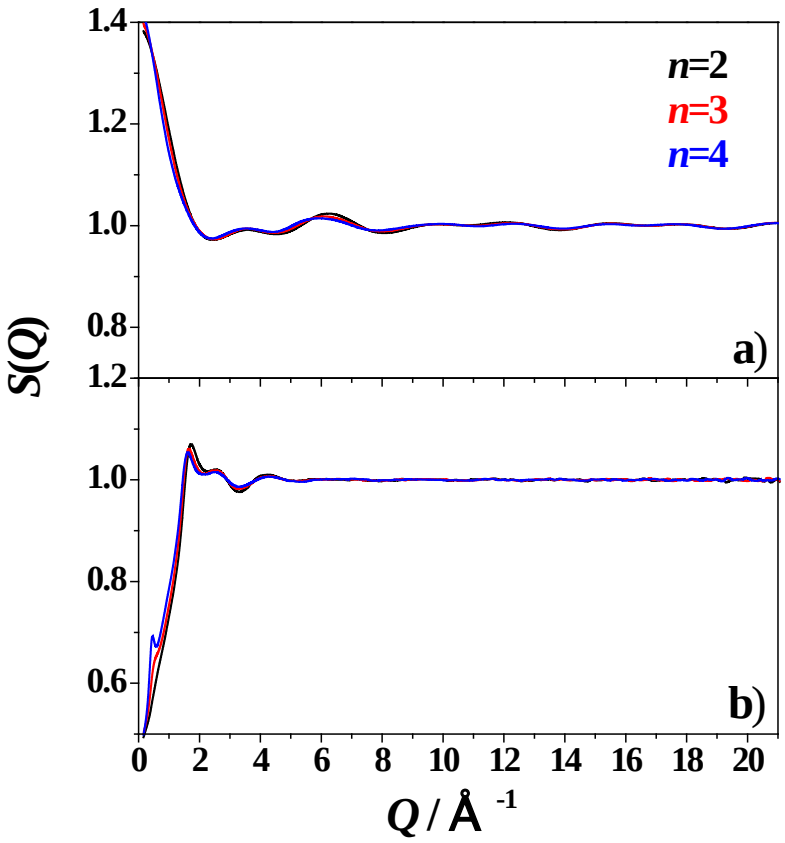

Figure S6. The intra- (a) and inter- (b) molecular structure factors obtained by the HEXRD experiments, $[C_2Am^+][NO_3^-]$ (black), $[C_3Am^+][NO_3^-]$ (red), and $[C_4Am^+][NO_3^-]$ (blue).

Figure S7.

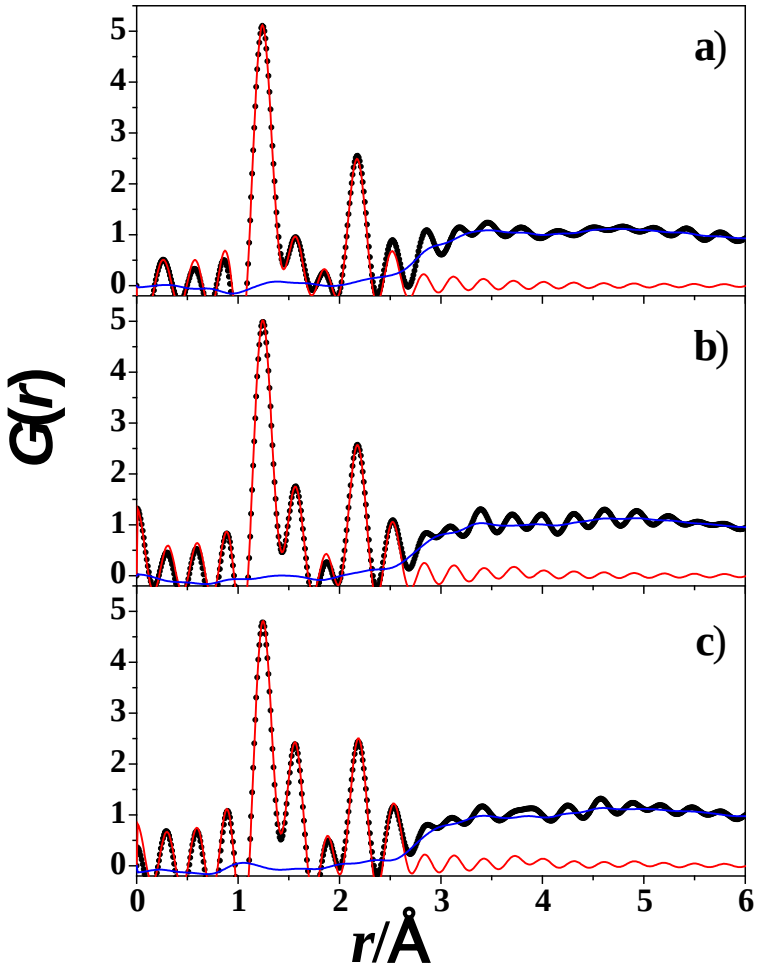

Figure S7. Total X-ray pair correlation function obtained by HEXRD experiments (black dots). The intra- and the inter-molecular X-ray pair correlation functions are also shown as red and blue lines, respectively for (a) $[C_2Am^+][NO_3^-]$, (b) $[C_3Am^+][NO_3^-]$, and (c) $[C_4Am^+][NO_3^-]$.

Figure S8.

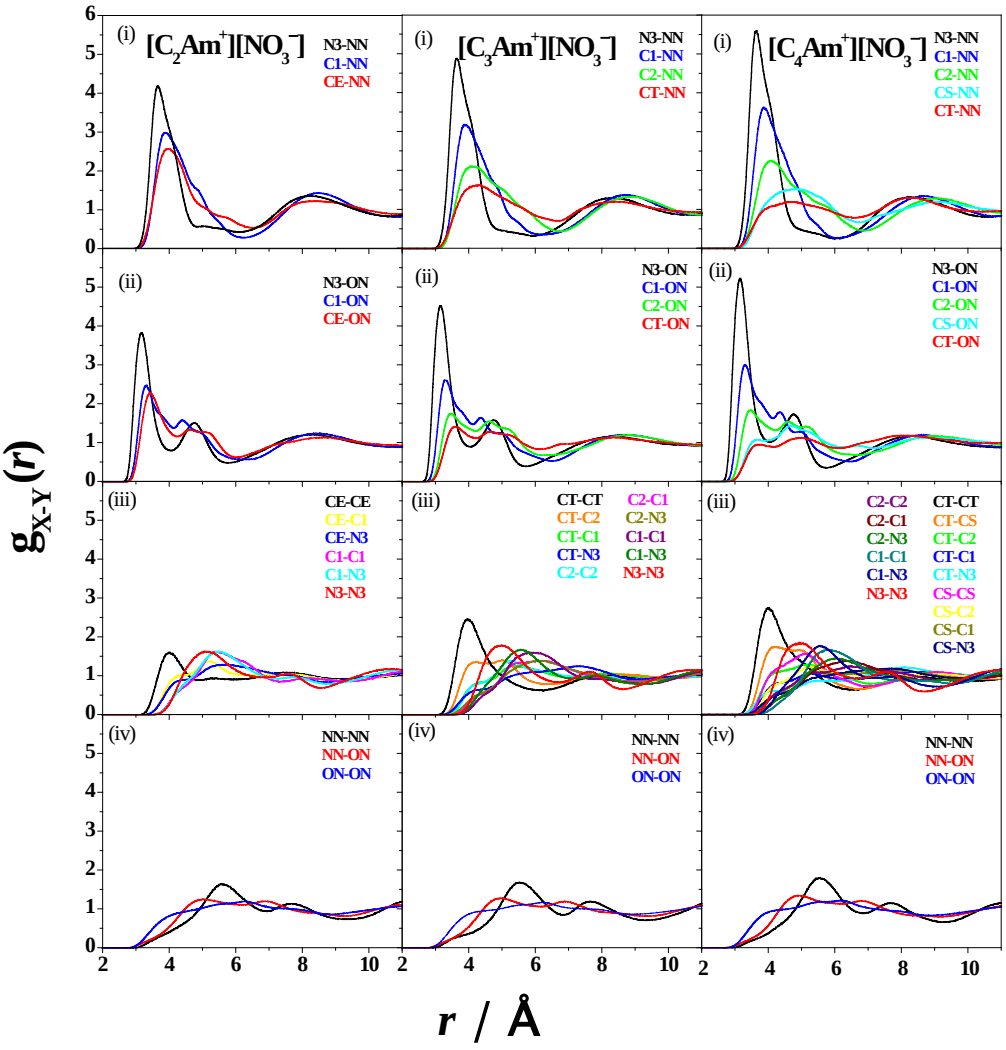

Figure S8. Partial atom-atom pair correlation function $g_{X\text{-}Y}(r)$ for the (i) cation-anion(NN), (ii) cation-anion(ON), (iii) cation-cation, (iv) anion-anion, respectively.

Figure S9.

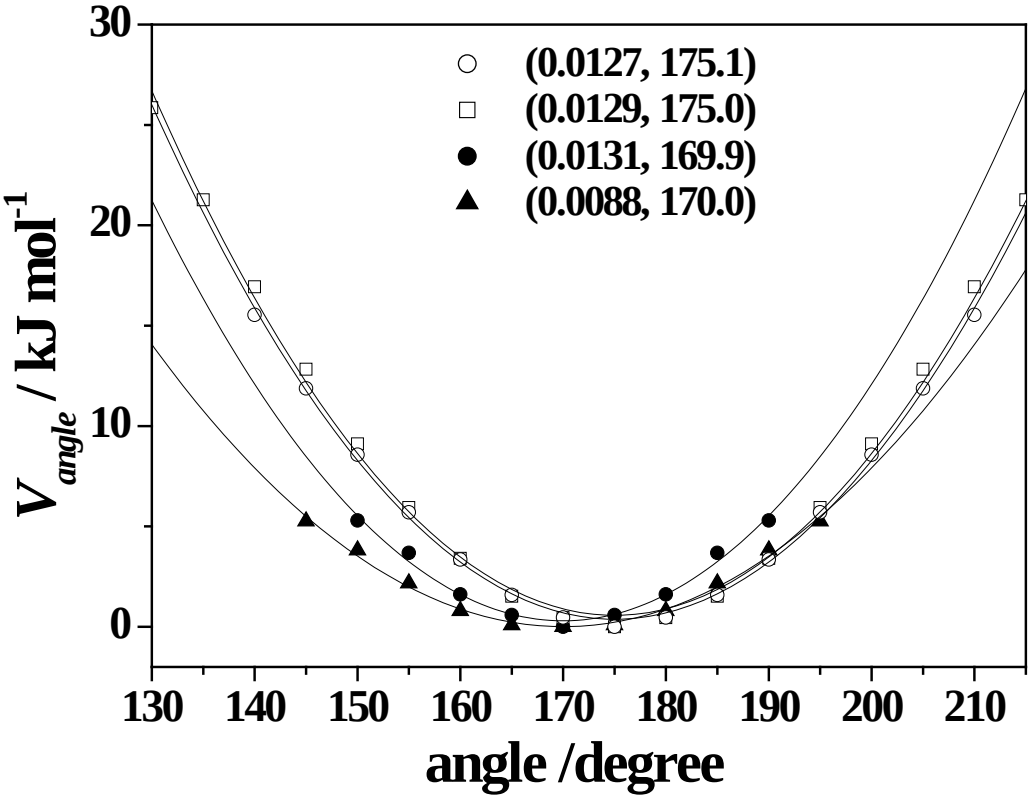

Figure S9. Potential energy surface (PES) as a function of the N-H-O bond angle, angle θ for $C_2H_5(H_2)N\cdots HONO_2$ molecular complexes in gas phase (○), in chloroform (□), and $C_2Am^+\cdots NO_3^-$ ion pairs in chloroform (●), in acetonitrile (▲). Solid lines represent calculated values with the refined parameters of k_θ and θ_0 using $V_{\text{angle}} = k_\theta(\theta - \theta_0)^2$, the values for which are shown in parentheses as ($k\theta$, θ_0).