SUPPLEMENTARY MATERIAL

Physical Chemistry Chemical Physics (PCCP)

Ammonium-Based Deep Eutectic Solvents for Sustainable CO_2 Capture: Insights from DFT, COSMO-RS, and MD Simulations

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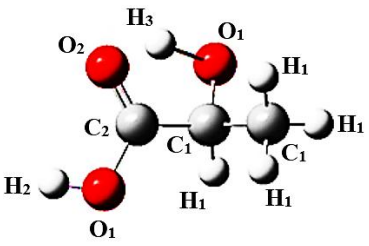
Table S1. Force field parameters for the studied DESs and also CO_2 molecule.

Lennard- Jones Parameters

Atoms	ε(kcal.mol^{-1})	σ(Å)
Cation		
C	0.055	3.875
H	0.022	2.352
N	0.200	3.296
Anion		
Cl	0.150	4.045
Lactic acid		
C_1	0.055	3.875
H_1	0.022	2.352
C_2	0.110	3.564
O_1	0.152	3.154
H_2	0.046	0.400
O_2	0.120	3.029
H_3	0.046	0.400
CO_2		
C	0.056	2.757
O	0.160	3.033



Bond Parameters

Bonds	K(kcal.mol^{-1}.Å^{-2})	r(Å)
Cation		
C - H	342.991	1.093
C-N	276.638	1.48
Lactic acid		
C_1-H_1	342.991	1.093
C_1-C_1	306.432	1.508
C_1-C_2	301.539	1.492
C_1-O_1	363.214	1.418
C_2-O_1	417.476	1.355
C_2-O_2	931.963	1.222
O_1-H_2	532.766	0.981
O_1-H_3	560.905	0.972
CO_2		
C-O	1029.995	1.160

Angle Parameters

Angles	K(kcal.mol^{-1}.rad^{-2})	θ(deg)
Cation		
H-C-H	37.134	108.836
H-C-N	62.754	106.224
C-N-C	62.034	112.251
Lactic acid		
H_1-C_1-C_1	45.770	110.549
H_1-C_1-C_2	46.778	108.385
H_1-C_1-O1	56.205	108.577
C_1-C_1-C_2	55.917	107.517
C_1-C_1-O_1	71.390	108.133
C_2-C_1-O_1	37.998	104.112
H_1-C_1-H_1	37.134	108.836
C_1-C_2-O_1	75.060	109.716
C_1-C_2-O_2	67.504	124.41
O_1-C2-O_2	83.120	124.425
C_2-O_1-H_2	41.956	111.948
C_1-O_1-H_3	57.069	106.503
CO_2		
O-C-O	55.999	180.000

Dihedral Parameters

Dihedrals	K(kcal.mol^{-1})	m	δ(deg)
Cation			
C-N-C-H	0.123	3	0
Lactic acid			
C_1-C_2-O_1-H_2	2.539	2	180
C_1-C_2-O_1-H_2	-0.583	1	0
C_1-C_2-O_1-H_2	-0.273	3	0
H_1-C_1-C_1-H_1	0.157	3	0
H_1-C_1-C_1-H_1	0.142	1	0
H_1-C_1-C_1-H_1	-0.693	2	180
H_1-C_1-C_2-O_1	0.165	3	0
H_1-C_1-C_2-O_1	-0.312	2	180
H_1-C_1-C_2-O_2	0.330	1	0
H_1-C_1-C_2-O_2	-0.704	2	180
H_1-C_1-C_2-O_2	0.154	3	0
H_1-C_1-O_1-H_3	0.298	1	0
H_1-C_1-O_1-H_3	-0.138	2	180

H_1-C_1-O_1-H_3	0.173	3	0
C_1-C_1-C_2-O_1	0.101	3	0
C_1-C_1-C_2-O_1	-0.167	2	180
C_1-C_1-C_2-O_1	-0.059	1	0
C_1-C_1-C_2-O_2	0.412	1	0
C_1-C_1-C_2-O_2	0.070	2	180
C_1-C_1-C_2-O_2	0.163	3	0
C_1-C_1-O_1-H_3	0.118	3	0
C_1-C_1-O_1-H_3	0.135	2	180
H_1-C_1-C_1-C_2	0.029	2	180
H_1-C_1-C_1-C_2	-0.128	1	0
H_1-C_1-C_1-O_1	0.140	3	0
H_1-C_1-C_1-O_1	0.536	2	180
H_1-C_1-C_1-O_1	-0.327	1	0
C_2-C_1-O_1-H_3	0.141	3	0
C_2-C_1-O_1-H_3	-0.830	2	180
C_2-C_1-O_1-H_3	-0.826	1	0
O_1-C_2-C_1-O_1	0.224	1	0
O_1-C_2-C_1-O_1	0.326	2	180
O_1-C_2-C_1-O_1	0.159	3	0
H_2-O_1-C_2-O_2	0.831	1	0
H_2-O_1-C_2-O_2	3.076	2	180
H_2-O_1-C_2-O_2	-0.029	3	0
O_2-C_2-C_1-O_1	0.365	2	180
O_2-C_2-C_1-O_1	-0.198	1	0
O_2-C_2-C_1-O_1	-0.070	3	180

Table S2. Comparison between the simulated densities of the studied DESs with experimental values[61] at 318.15 K and 1 atm with confidence intervals expressed as ±σ.

Systems	ρ^{Exp}(g.cm^{-3})	ρ^{Simu}(g.cm^{-3})	%dev
DES(1)	1.1274	1.1027±0.0052	2.19
DES(2)	1.0958	1.1076±0.0035	-1.08
DES(3)	1.0080	1.0393±0.0023	-3.11

Table S3. Interaction energies with dispersion (D3) and basis set superposition error (BSSE) corrections for the studied DES–CO_2 systems and their corresponding isolated DES and CO_2 molecules obtained using the PCM model.

	opt	BSSE	D3	$E_{Correct}$	E_{abs} (a.u.)	E_{abs} (kcal.mol^{-1})
DES(1)	-1362.2042	0.0025	-0.0413	-1362.2430	----	----
DES(2)	-1519.5073	0.0033	-0.0561	-1519.5601	----	----
DES(3)	-1834.1019	0.0038	-0.0835	-1834.1816	----	----
CO_2	-188.6496	----	-0.0002	-188.6498	----	----
			DES(1) - CO_2			
(1)	-1550.8664	0.0035	-0.0433	-1550.9062	-0.0134	-8.4086
(2)	-1550.8665	0.0030	-0.0423	-1550.9058	-0.0130	-8.1576
(3)	-1550.8651	0.0031	-0.0407	-1550.9027	-0.0099	-6.2123
(4)	-1550.8661	0.0035	-0.0425	-1550.9051	-0.0123	-7.7184
			DES(2) - CO_2			
(1)	-1708.1579	0.0039	-0.0609	-1708.2149	-0.0050	-3.1375
(2)	-1708.1575	0.0037	-0.0589	-1708.2127	-0.0028	-1.7570
(3)	-1708.1577	0.0040	-0.0601	-1708.2138	-0.0039	-2.4473
(4)	-1708.1571	0.0035	-0.0567	-1708.2103	-0.0004	-0.2510
			DES(3) - CO_2			
(1)	-2022.7523	0.0041	-0.0857	-2022.8339	-0.0025	-1.5688
(2)	-2022.7525	0.0046	-0.0882	-2022.8361	-0.0047	-2.9493
(3)	-2022.7524	0.0042	-0.0853	-2022.8335	-0.0021	-1.3178
(4)	-2022.7512	0.0044	-0.0861	-2022.8329	-0.0015	-0.9413

Figure caption

Figure S1. IR spectra of the studied DESs, showing the contributions of cation, anion, LA, and CO_2 molecules in the DES–CO_2 systems.

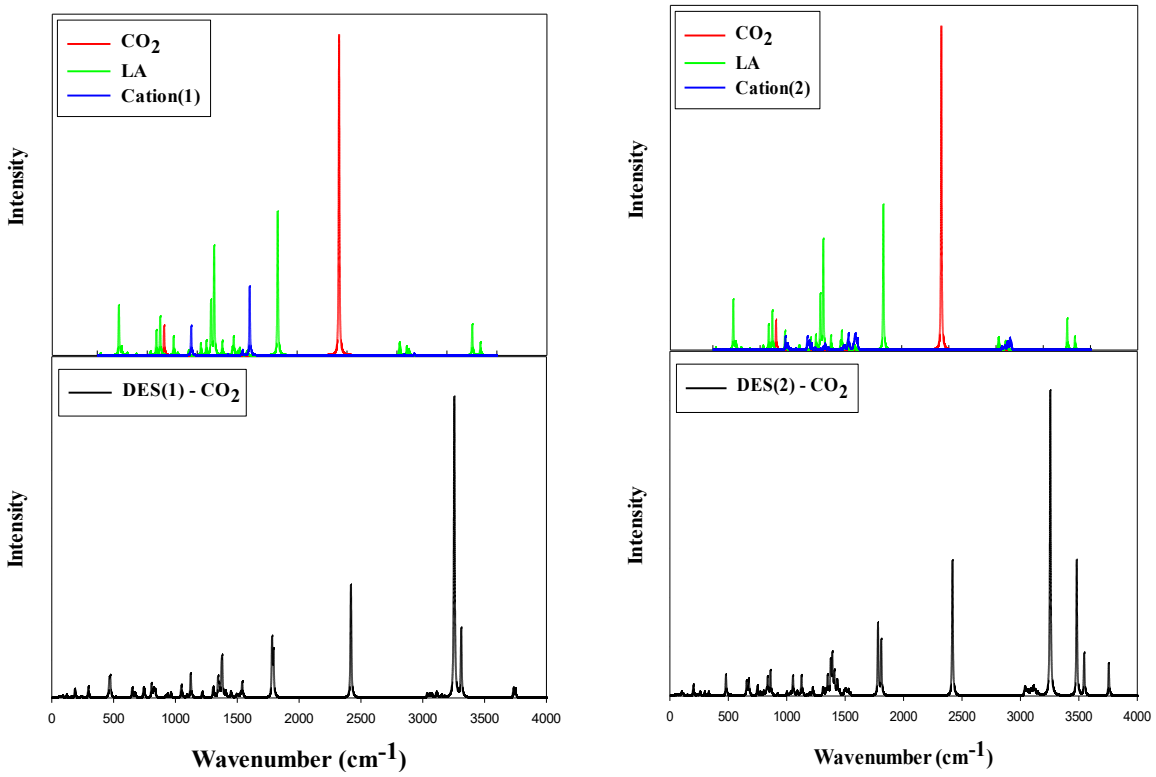
Figure S2. Comparison of the spatial distribution of the centers of mass (COMs) of the cation, anion, and LA molecules around CO_2 with increasing alkyl chain length, from the DES(1)–CO_2 to the DES(3)–CO_2 systems.

Figure S3. Comparison of the distance distribution of the first five neighboring CO_2 molecules from the reference cation with increasing alkyl chain length in the DES(1)–CO_2 and DES(3)–CO_2 systems.

Figure S4. Mean square displacement (MSD) plots of cation, anion, LA, and CO_2 particles of the studied DESs at 500 K and at 1 atm. The evolution of β parameter with time has been also shown in each plot.

Figure S5. Self-part of the van Hove correlation functions for the cation, anion, LA, and CO_2 molecules in the studied DES–CO_2 systems.

Figure S1.


CO2
LA
Cation(1)
DES(1) - CO2
Intensity
Wavenumber (cm-1)
CO2
LA
Cation(2)
DES(2) - CO2
Intensity
Wavenumber (cm-1)

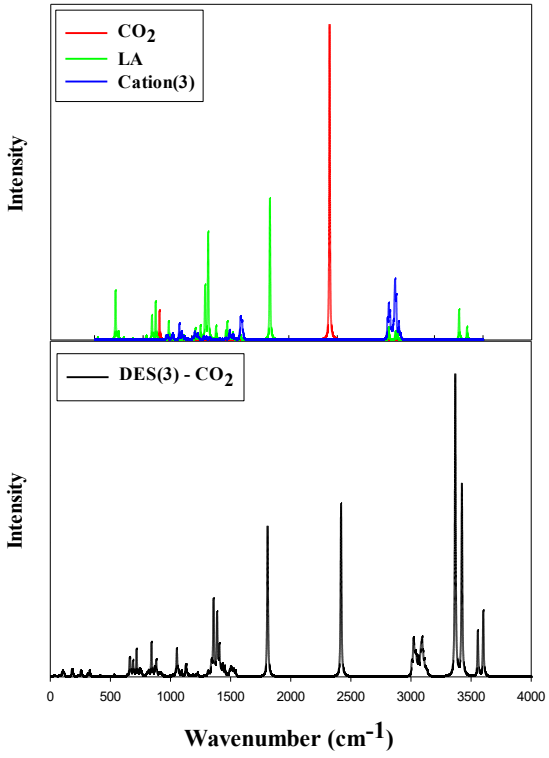

CO2
LA
Cation(3)
DES(3) - CO2
Intensity
Wavenumber (cm-1)

Figure S2.

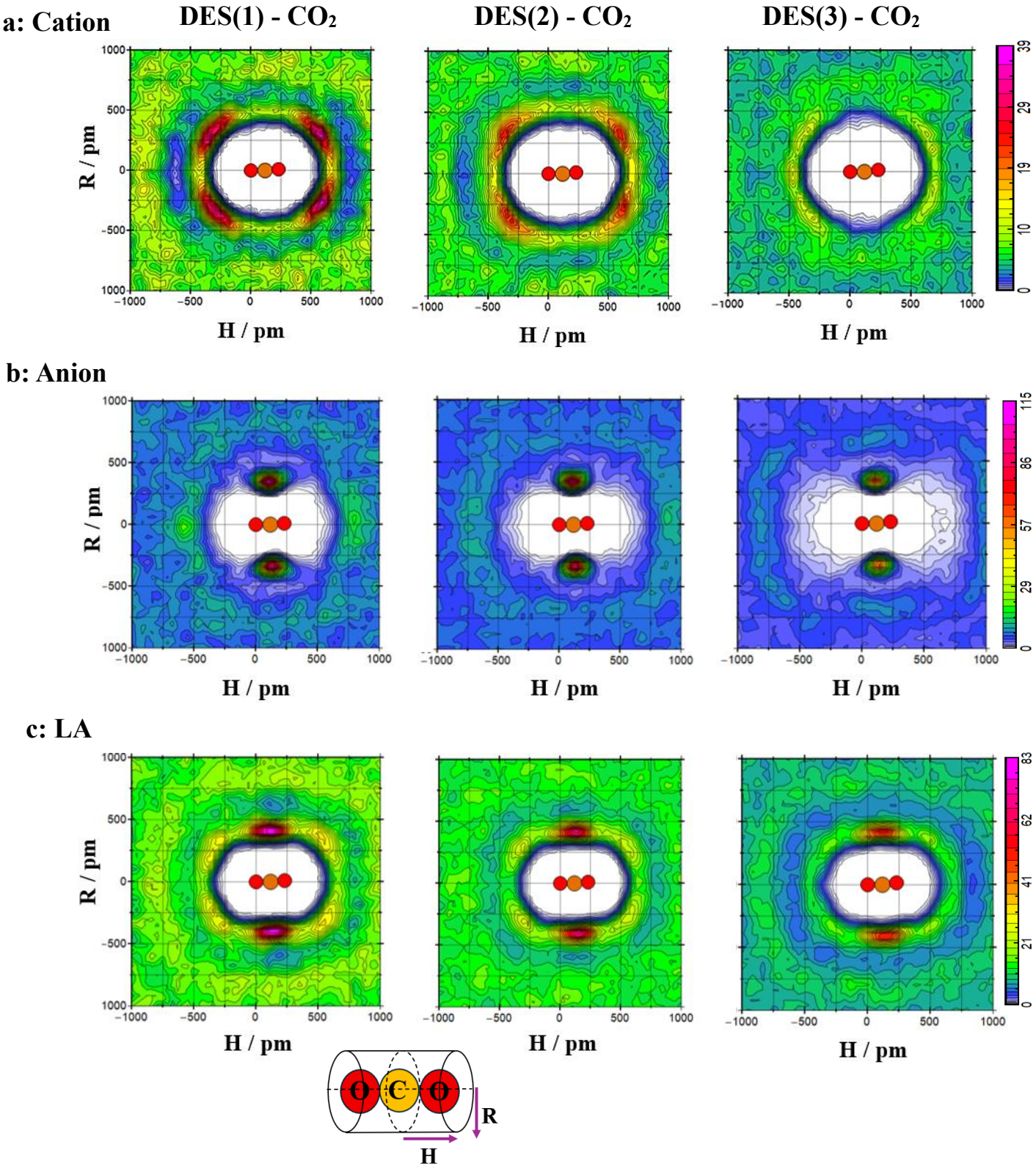


Figure S3.

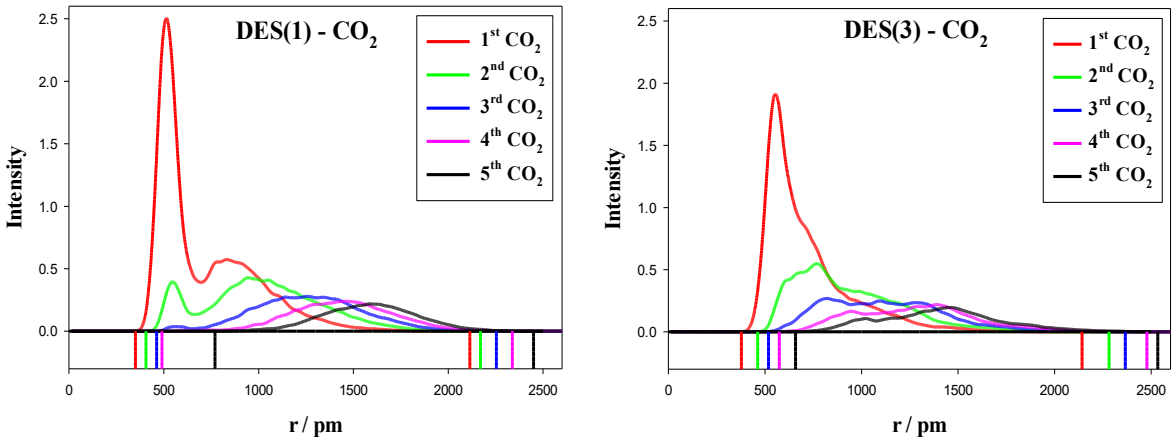

DES(1) - CO2
1st CO2
2nd CO2
3rd CO2
4th CO2
5th CO2
Intensity
r / pm
DES(3) - CO2
1st CO2
2nd CO2
3rd CO2
4th CO2
5th CO2
Intensity
r / pm

Figure S4.

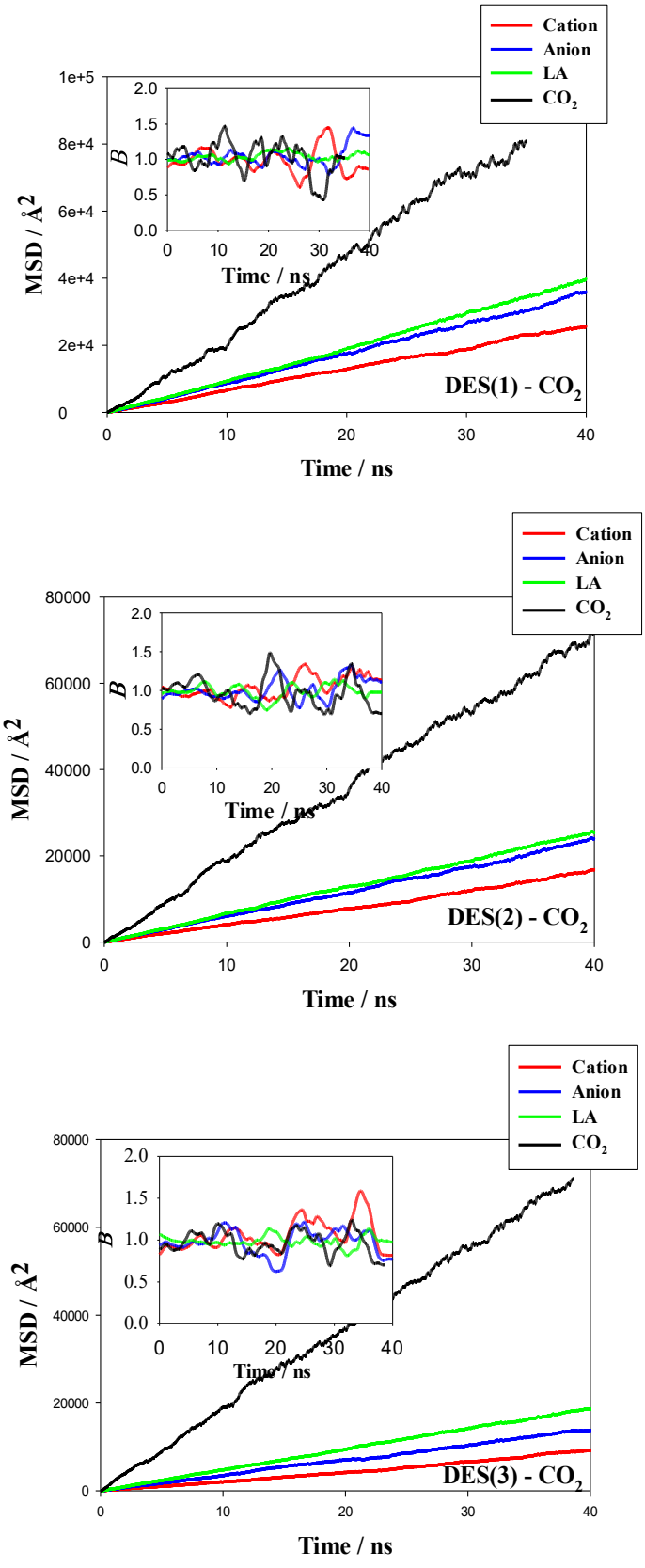
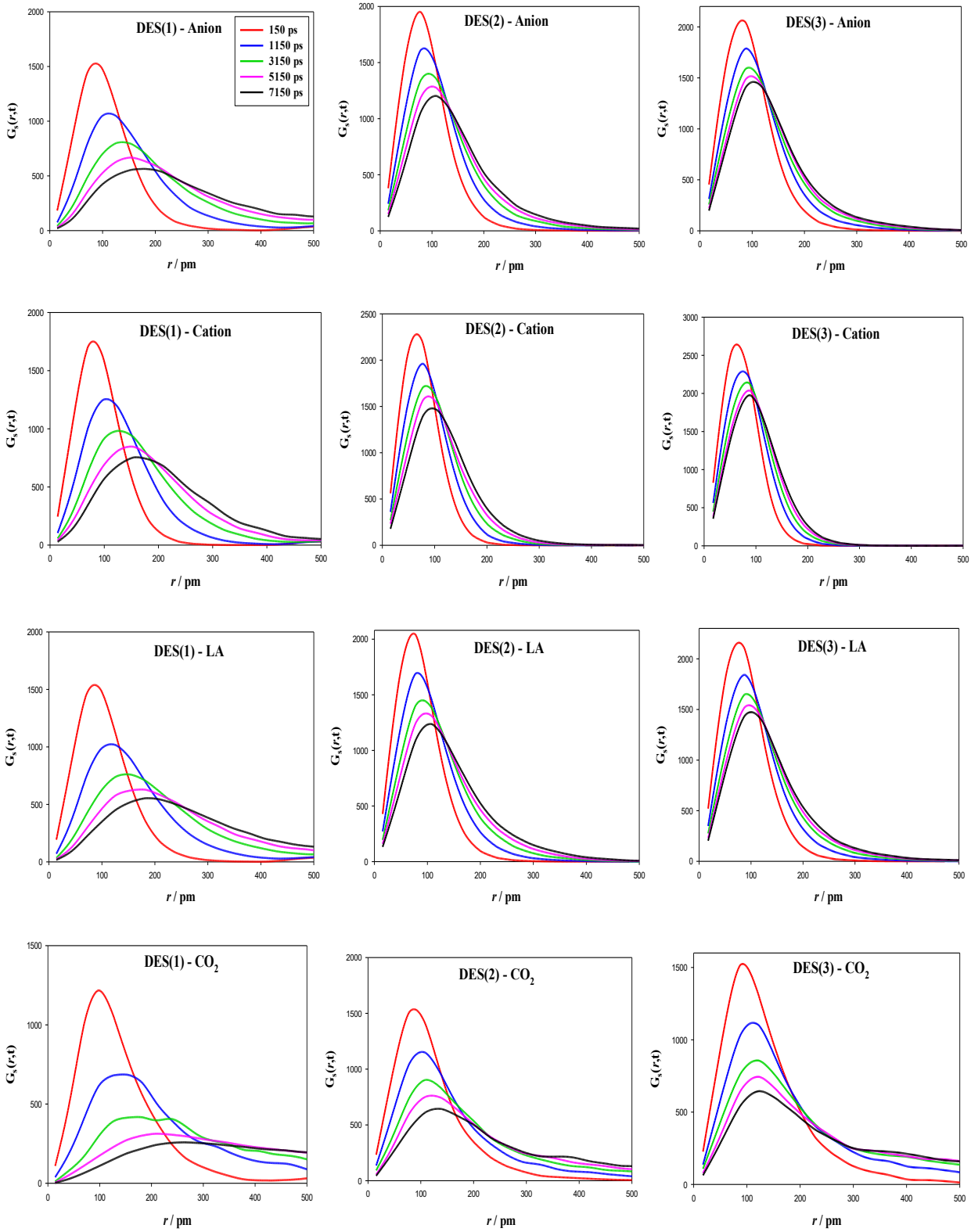


Figure S5.


DES(1) - Anion
150 ps
1150 ps
3150 ps
5150 ps
7150 ps
DES(2) - Anion
DES(3) - Anion
DES(1) - Cation
DES(2) - Cation
DES(3) - Cation
DES(1) - LA
DES(2) - LA
DES(3) - LA
DES(1) - CO2
DES(2) - CO2
DES(3) - CO2
Gs(r,t)
r / pm