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

Supplementary Information: Adsorption-Induced Clustering of CO_2 on Graphene

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Table S1: Force-field parameters of the two-site model for nitrogen gas molecule proposed by Chae and Violi [J. Chem. Phys. 134, 044537 (2011)].

	q [e]	σ [nm]	ϵ [kJ/mol]	bond [nm]	K_b [kJ/mol·nm^2]
N_2	0.0	0.32973	0.30198	0.1085	1354950.0

Table S2: Adsorption energy, per molecule, of a dimer of CO_2, N_2, and CH_4 on the surface of $C_{24}H_{12}$ and $C_{96}H_{24}$ using the B3LYP-D/6-31+G* level of calculation. More specifically, we calculate the adsorption energy by $E_{ads} = (E_{PAH+X_2} - E_{PAH} - E_{X_2})/2$, where X_2 is the dimer of X. All values are given in kJ/mol.

	$C_{24}H_{12}$	$C_{96}H_{24}$
CO_2	-17.2	-21.3
N_2	-12.6	-15.5
CH_4	-12.1	-15.1

Table S3: The value of the LJ-parameter $\epsilon(C_{gra}–i_{gas})$ between the carbon atoms of graphene and any atom of the three gases, for the different scalings, χ_{g-g}, of the interaction energy between the graphene and the gases. Thus, χ_{g-g}=1.0 corresponds to the unmodified force-field. All values are reported in kJ/mol.

χ_{g-g}	$\epsilon(C_{gra}–C_{CO_2})$	$\epsilon(C_{gra}–O_{CO_2})$	$\epsilon(C_{gra}–N_{N_2})$	$\epsilon(C_{gra}–C_{CH_4})$	$\epsilon(C_{gra}–H_{CH_4})$
1.0	0.31414	0.53735	0.36475	0.34841	0.23490
0.9	0.28273	0.48362	0.32828	0.31357	0.21141
0.8	0.25131	0.42988	0.29180	0.27873	0.18792
0.7	0.21990	0.37615	0.25533	0.24389	0.16443
0.6	0.18849	0.32241	0.21885	0.20905	0.14094
0.5	0.15707	0.26868	0.18238	0.17421	0.11745
0.4	0.12566	0.21494	0.14590	0.13937	0.09396
0.3	0.09424	0.16121	0.10943	0.10452	0.07047

Table S4: Equilibrium constant for adsorption, $K(x)=\rho_{2D,\,ad}/\rho_{3D,\,bulk}$, for x=$CO_2$, N_2, and CH_4. The results are taken from both the ternary (T) and binary (B) gas-mixture simulations for different scalings, χ_{g-g}, of the graphene–gases interaction energies. The values of K are given in nm.

	T: CO_2+N_2+CH_4			**B: CO_2+N_2**		**B: CO_2+CH_4**	
χ_{g-g}	K(CO_2)	K(N_2)	K(CH_4)	K(CO_2)	K(N_2)	K(CO_2)	K(CH_2)
1.0	20.86	2.67	3.29	27.13	3.83	24.16	1.23
0.9	15.88	2.51	3.11	—	—	—	—
0.8	11.18	2.24	2.81	—	—	—	—
0.7	7.19	1.83	2.34	—	—	—	—
0.6	4.20	1.35	1.76	—	—	—	—
0.5	2.30	0.93	1.23	—	—	—	—
0.4	1.25	0.63	0.82	—	—	—	—
0.3	0.70	0.44	0.54	0.73	0.46	0.70	0.18

Table S5: The interaction energy between the same-type gas molecules, u_{x-x}, adsorbed on graphene for the ternary gas mixture simulations at different scalings of the graphene-gas interaction strength, χ_{g-g}. All energies are given in kJ/mol.

χ_{g-g}	$u_{CO_2-CO_2}$	$u_{N_2-N_2}$	$u_{CH_4-CH_4}$
1.0	-2.8	-1.4	-0.4
0.9	-2.4	-1.3	-0.3
0.8	-1.9	-1.2	-0.3
0.7	-1.4	-1.1	-0.2
0.6	-0.9	-0.8	-0.2
0.5	-0.6	-0.6	-0.1
0.4	-0.3	-0.4	-0.1
0.3	-0.2	-0.3	-0.1

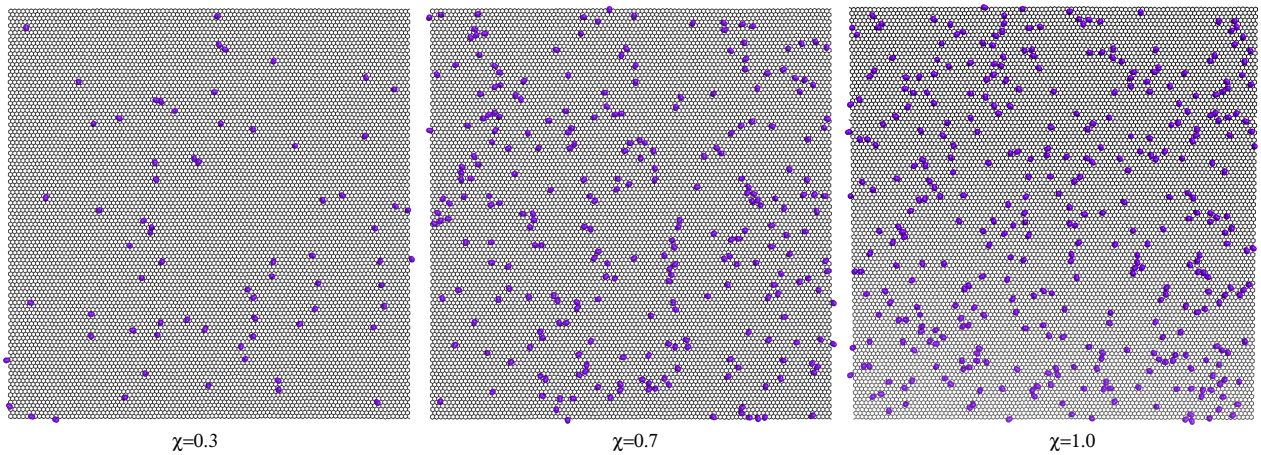

Figure S1: A top-view projection onto one of the graphene sheets of the adsorbed nitrogen molecules for the ternary gas mixture system with graphene-gas interaction strength of χ_{g-g}=0.3, 0.7, and 1.0. For clarity, carbon dioxide and methane molecules are not shown here (see Fig. 5 and Fig. S2). Graphene is shown as black sticks and N_2 molecules as purple spheres.

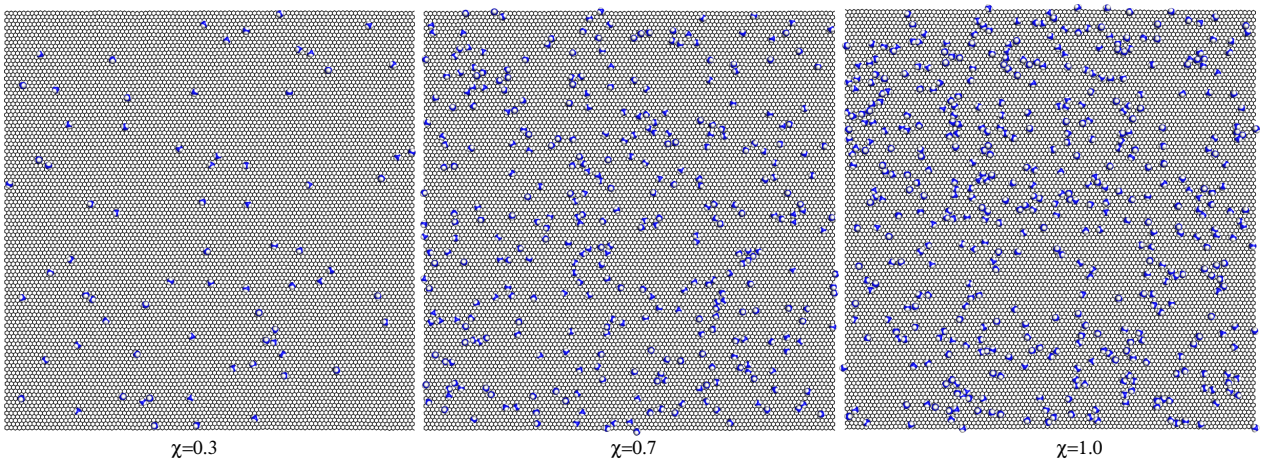

Figure S2: Same as Fig. 5 and Fig. S1 but for the methane molecules.

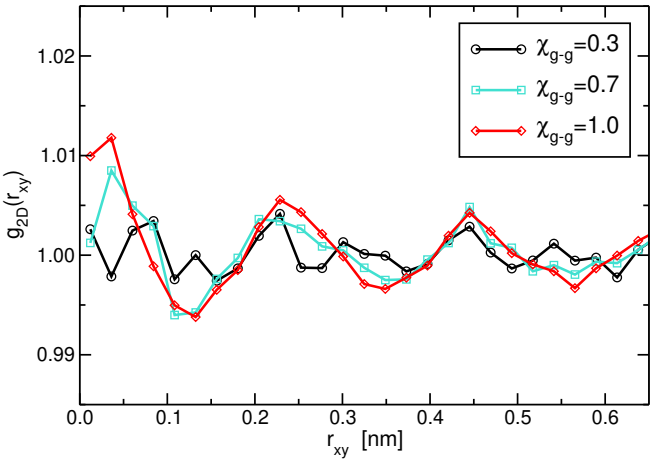

Figure S3: Two-dimensional radial distribution functions, projected on the xy-plane, between the carbon atoms of adsorbed CO_2 molecules and the carbons of the graphene sheet on which the CO_2 molecules are adsorbed, for three different scalings of the graphene-gas interaction energy.