On the reason for the increased solubility of CO_2 in $[C_nMIM][NTf_2]$ ionic liquids.

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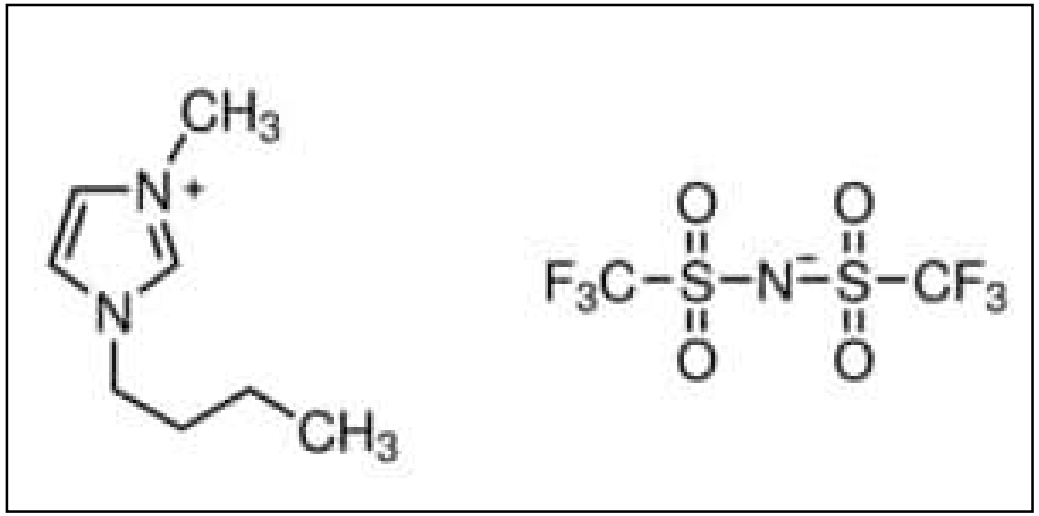
Introduction



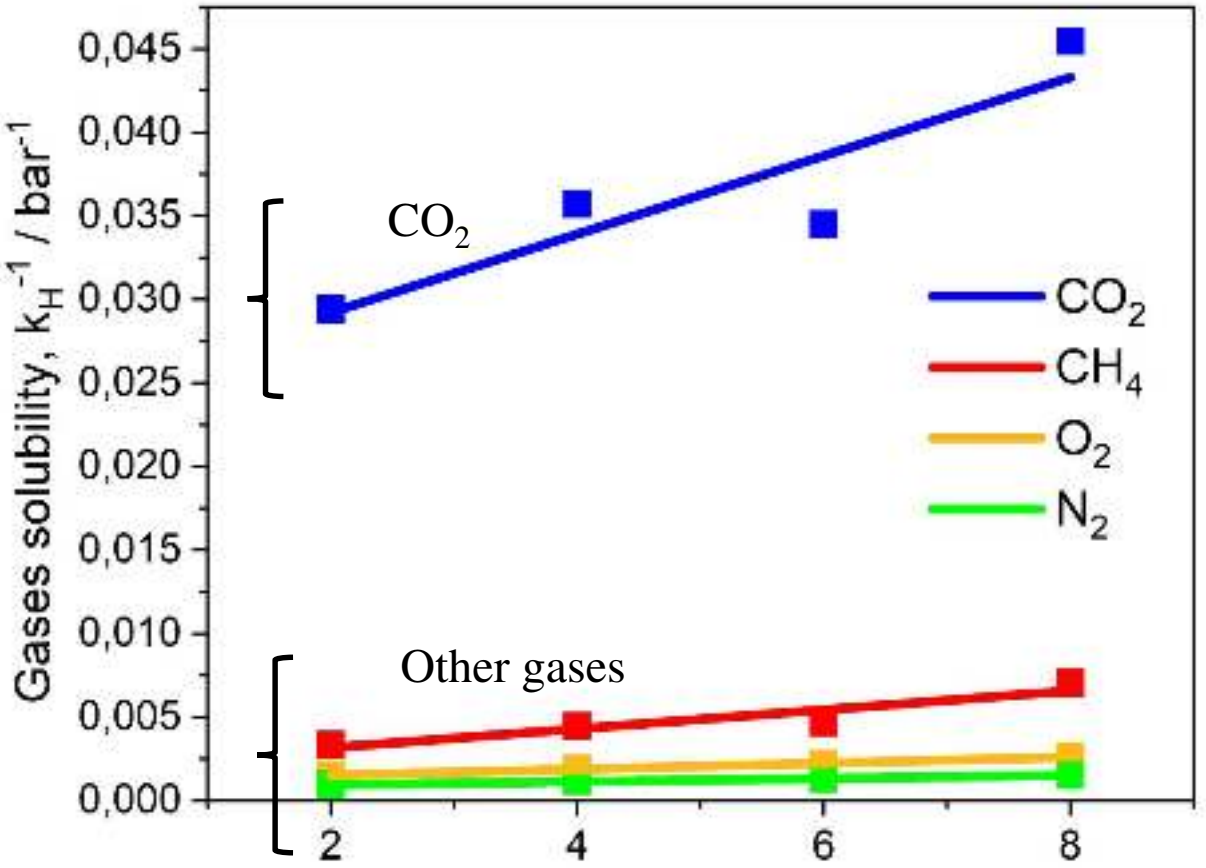
1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_nMIM][NTf_2]$)

Ionic liquids (ILs) are salts in the liquid state with melting point below 100 °C

Ionic liquids (ILs) possess several unique properties, for example:

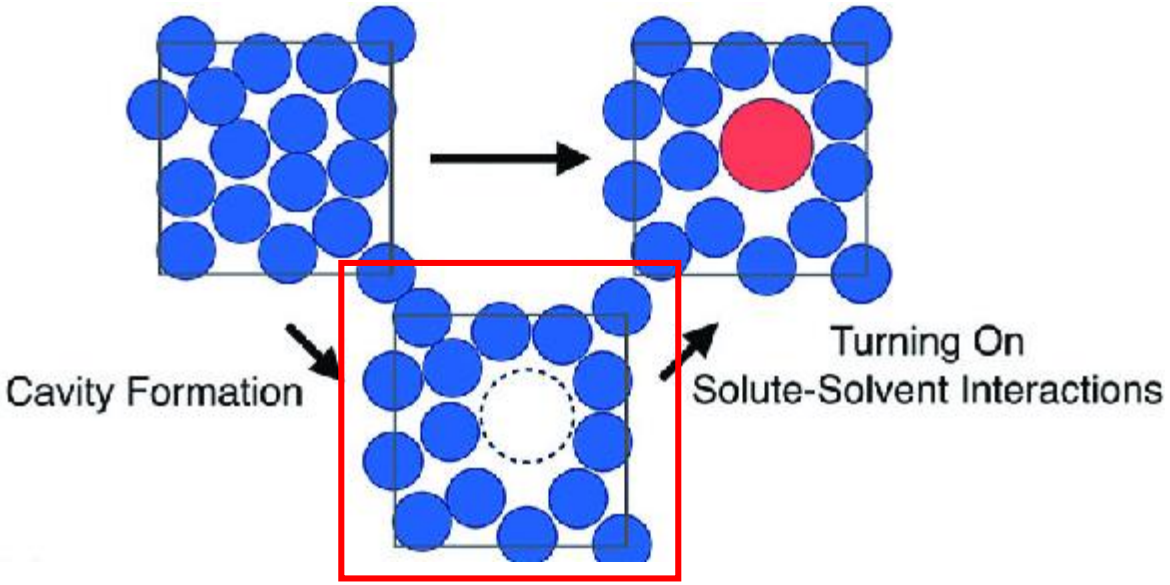
- High thermal stability
- Low volatility
- Wide range of temperatures at which they are in a liquid state

An important property of ILs is the high selectivity of CO_2 dissolution. Solubility of CO_2 in ILs is significantly higher than the solubility of other gases, such as N_2, CH_4, O_2, Xe, and CO.



Gases solubility in [C_nMIM][NTF_2] IL. Data is taken from Kerlé et al. PCCP (2017): 1770-1780., for 300 K.

Connection between empty volume and the solubility of gases



Kenji, Mochizuki & Sumi, Tomonari & Koga, Kenichiro. (2017). Influence of Co-non-solvency on Hydrophobic Molecules Driven by Excluded Volume Effect. Phys. Chem. Chem. Phys.. 19. 10.1039/C7CP04152G.

The solubility is determined both by the interaction of the dissolved molecule with the solvent and the presence of an empty volume necessary for its placement.

Solubility of gases in ILs is largely determined by empty volume:

- Gases solubility increases with an increase in free volume fraction (FFV) in ILs
- The solubility of CO_2 in ILs with the $[NTf_2]$ anion is higher than in ILs with $[PF_6]$ or $[BF_4]$ anions, although the interaction of CO_2 with the latter is stronger than with $[NTf_2]$.

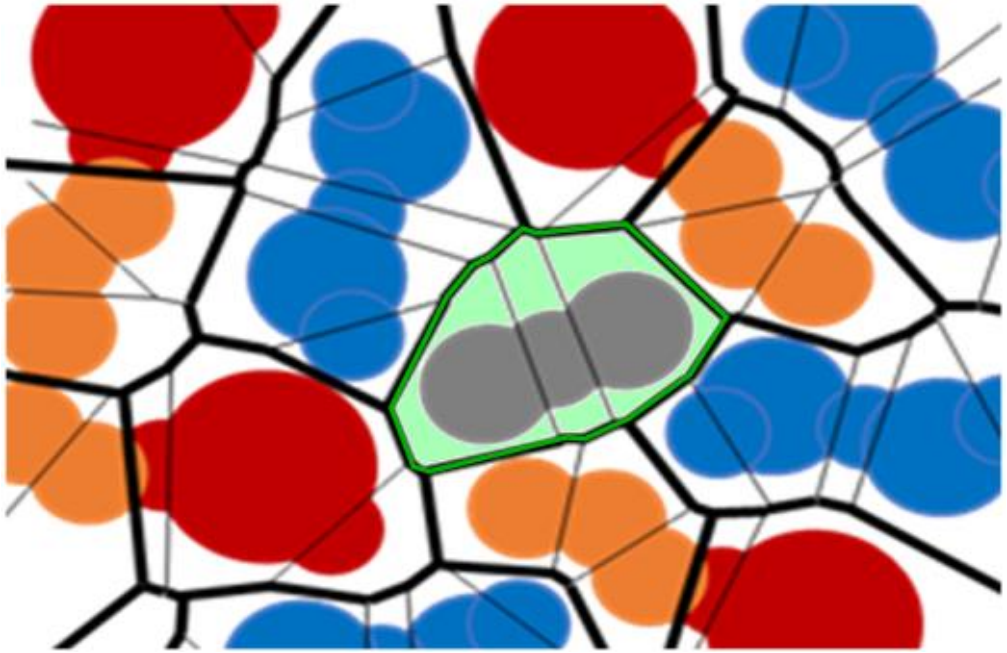
Intermolecular voids are important for the solubility of gases in ionic liquids

- CO_2 solubility in ILs significantly higher than other gases, such as O_2, N_2, CH_4.
- Intermolecular voids affect the solubility of gases in ionic liquids.
- Does the structure of the CO_2 solutions differ?

Aim: to study the structure of CO_2, O_2, N_2, and CH_4 solutions in ionic liquids. Particular attention is paid to the change in empty volume during dissolution.

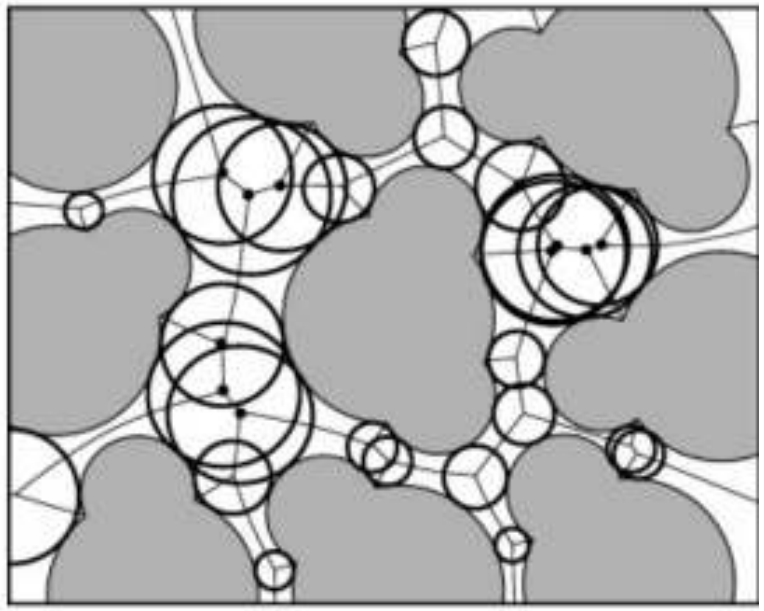
Voronoi-Delaunay method

The Voronoi tessellation determines the region closest to a given molecule - ***Voronoi region of the molecule.***



Voronoi tessellation

The Delaunay tessellation gives empty spheres inscribed between the atoms of the system - ***interstitial spheres.***



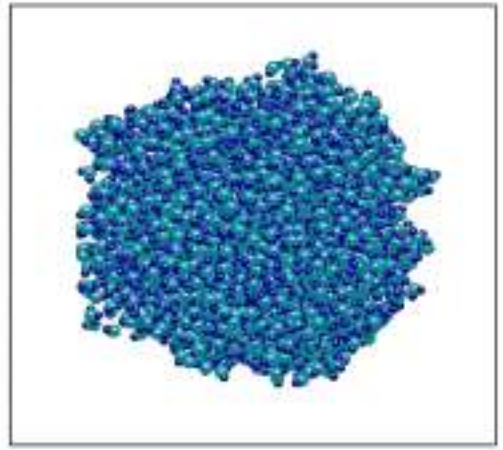
Interstitial spheres

Interstitial spheres characterize the voids of the system: the spheres with large radii indicate the presence of large cavities.

Molecular dynamics (MD)

Numerical solution of classical equations of motion for a system with large number of interacting particles (atoms).

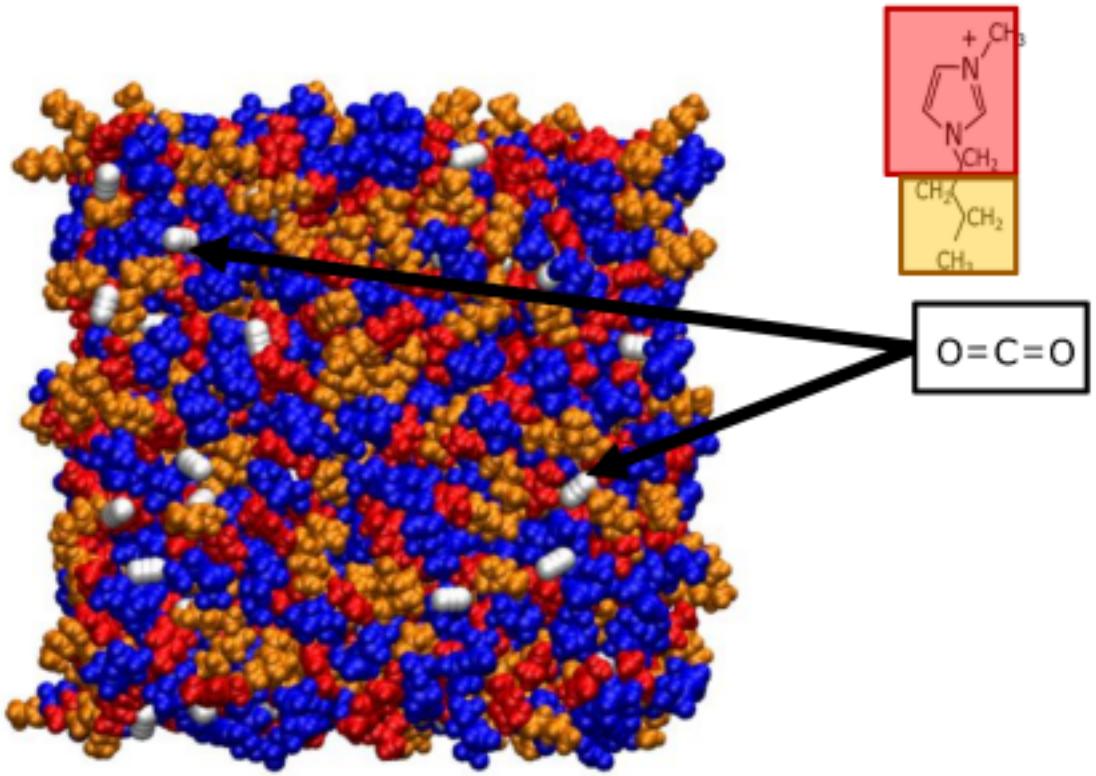
The result of the MD calculations is a set of coordinates and velocities of atoms, reflecting the time evolution of the system.

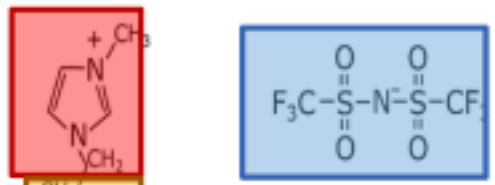


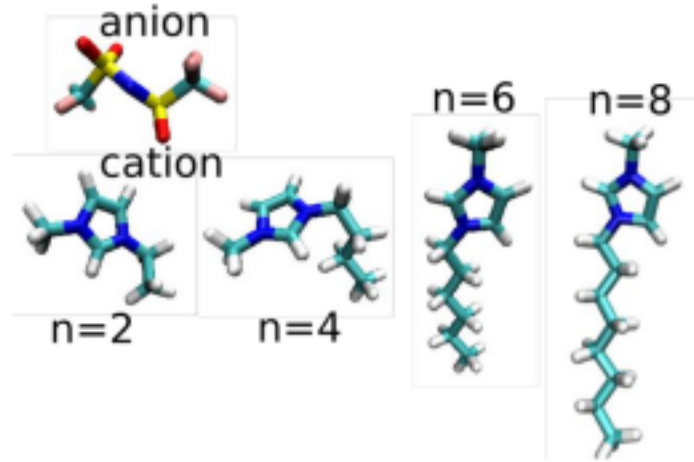
t	$t+\delta t$	$t+2\delta t$	…	$t+n\delta t$
x_1,y_1,z_1 x_2,y_2,z_2 … x_N,y_N,z_N	x_1,y_1,z_1 x_2,y_2,z_2 … x_N,y_N,z_N	x_1,y_1,z_1 x_2,y_2,z_2 … x_N,y_N,z_N	…	x_1,y_1,z_1 x_2,y_2,z_2 … x_N,y_N,z_N
v^x_1,v^y_1,v^z_1 v^x_2,v^y_2,v^z_2 … v^x_N,v^y_N,v^z_N	v^x_1,v^y_1,v^z_1 v^x_2,v^y_2,v^z_2 … v^x_N,v^y_N,v^z_N	v^x_1,v^y_1,v^z_1 v^x_2,v^y_2,v^z_2 … v^x_N,v^y_N,v^z_N	…	v^x_1,v^y_1,v^z_1 v^x_2,v^y_2,v^z_2 … v^x_N,v^y_N,v^z_N

MD simulations

All-atom models of the mixtures of CO_2, O_2, N_2, CH_4 molecules in $[C_nMIM][NTF_2]$ IL were obtained.



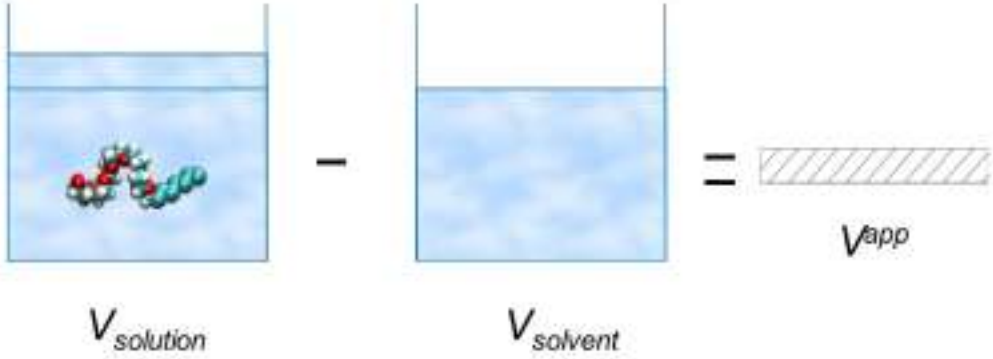




1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

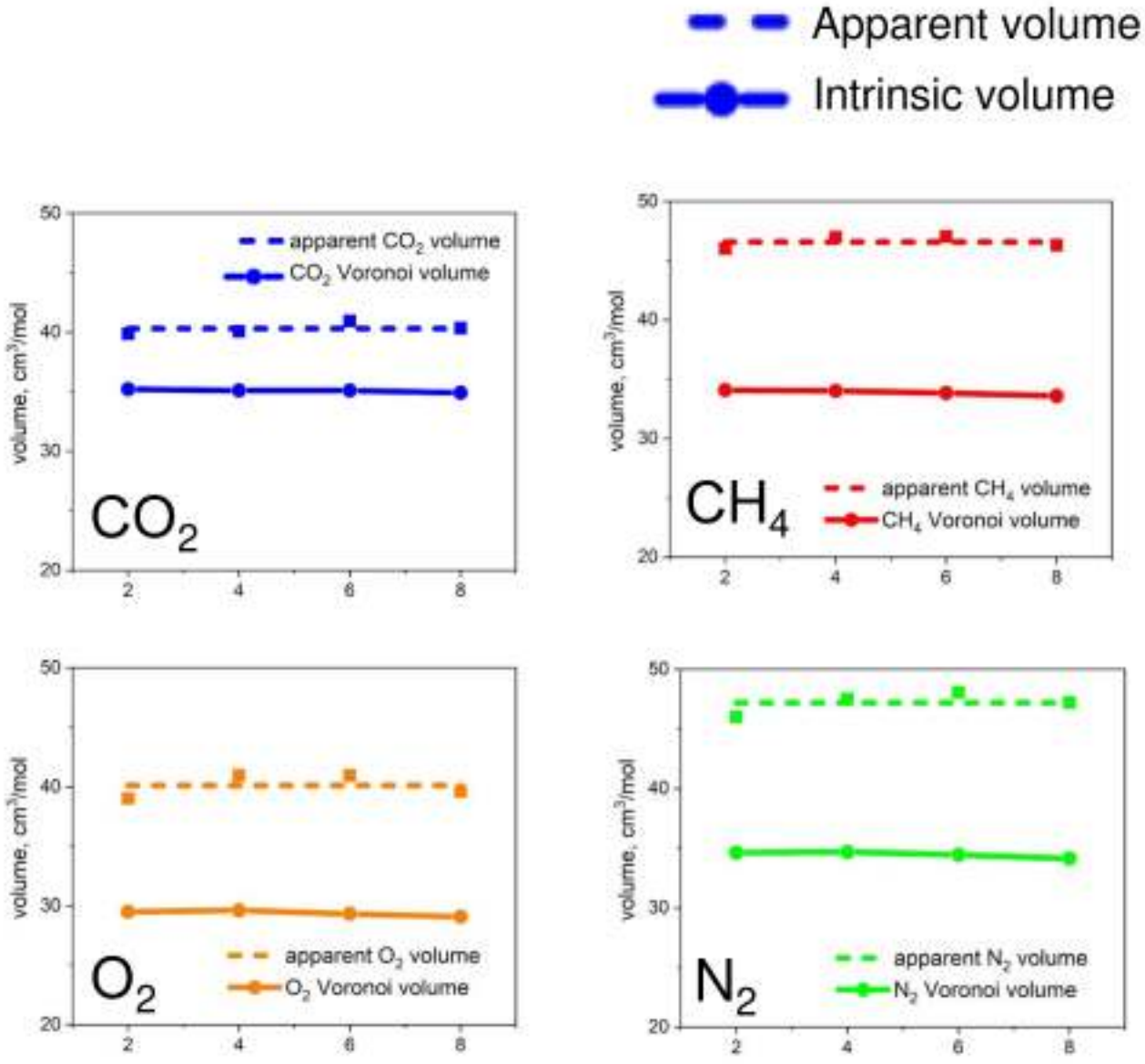
MD simulations. Gromacs 2019.4. 512 ion pairs. 100 gas molecules. NPT ensemble, pressure 10 bar, temperature 293 K.

Results. Apparent volume



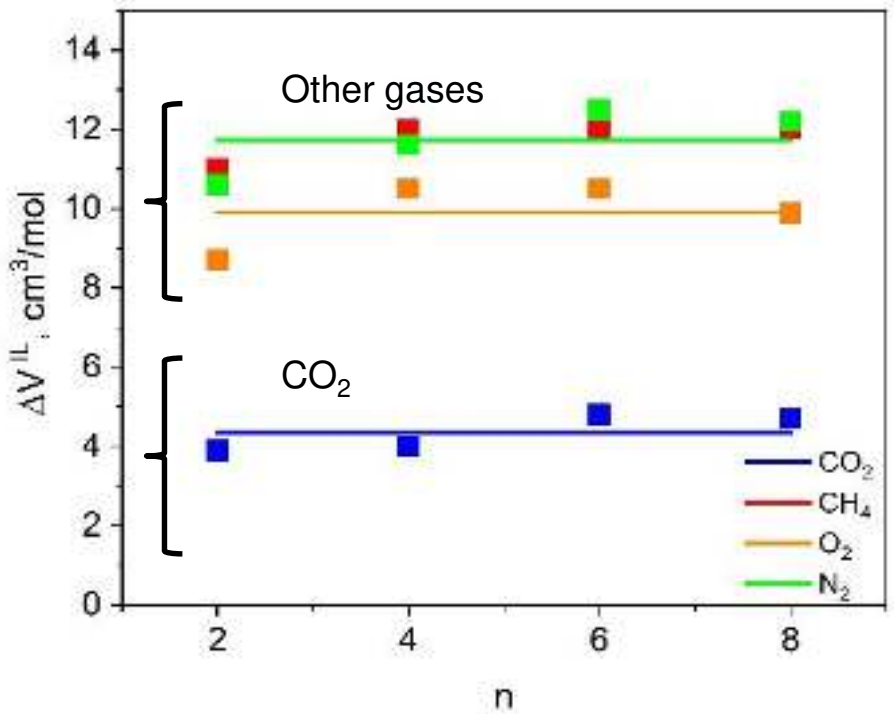
$$V_a = V^{gas} + \Delta V^{IL}$$

Apparent volume for all gases exceeds their intrinsic volume i.e. dissolved gas molecules create an additional empty volume in the mixture, loosening the IL. However, the CO_2 molecule adds a significantly smaller empty volume compared to O_2, N_2, and CH_4 molecules.



Apparent and intrinsic volumes of the gases in the ILs.

How much empty volume do the dissolved molecules contribute to the IL?

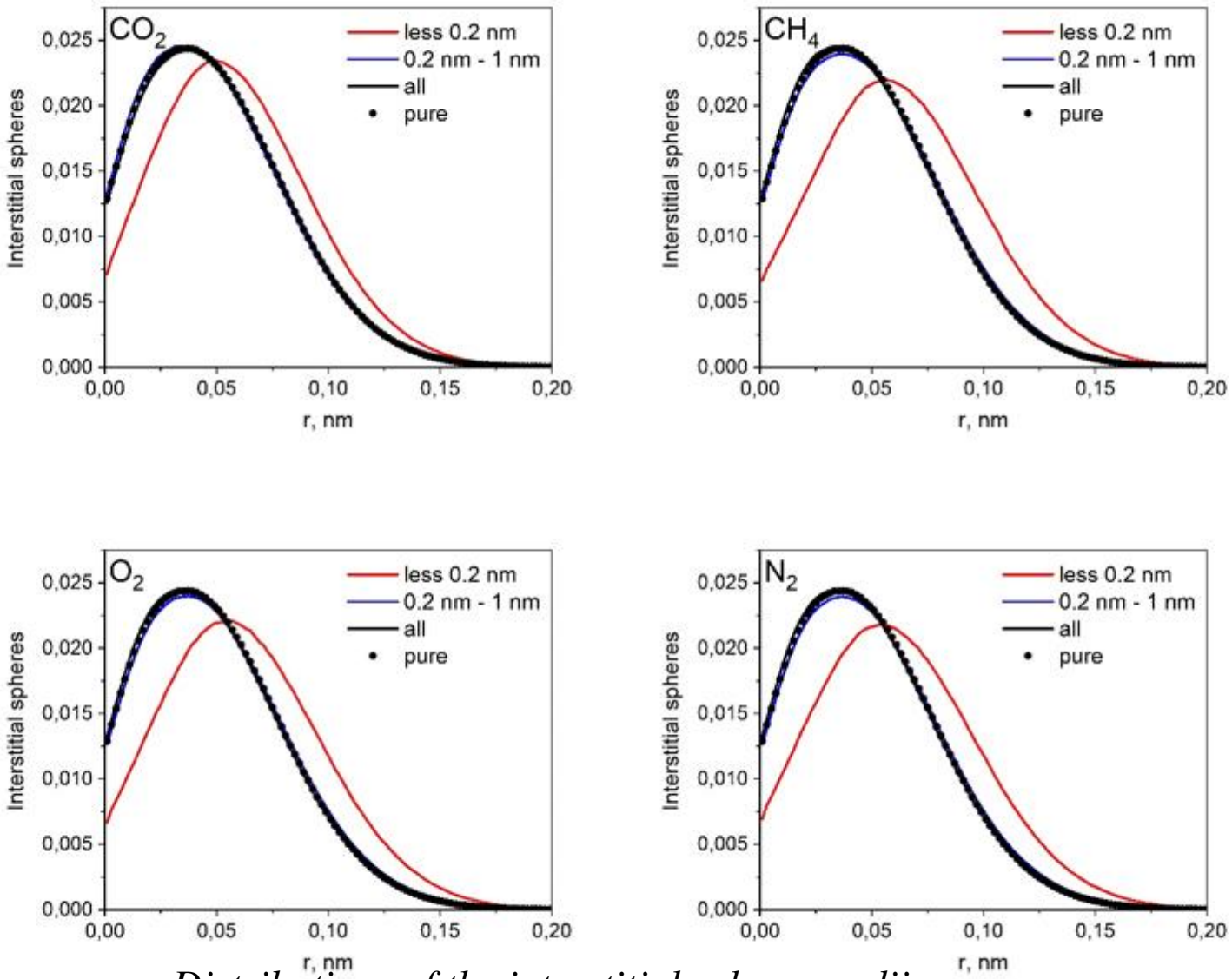


$$V_a = V^{gas} + \Delta V^{IL}$$

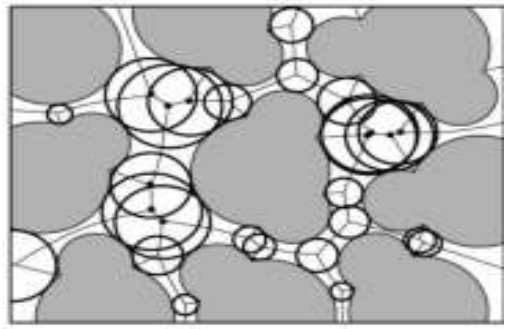
Change in the volume of the IL, ΔV^{IL}, depending on the length of the alkyl substituent n for different dissolved gases

O_2, N_2, and CH_4 molecules add a significantly more empty volume compared to CO_2.

Where do additional voids appear?



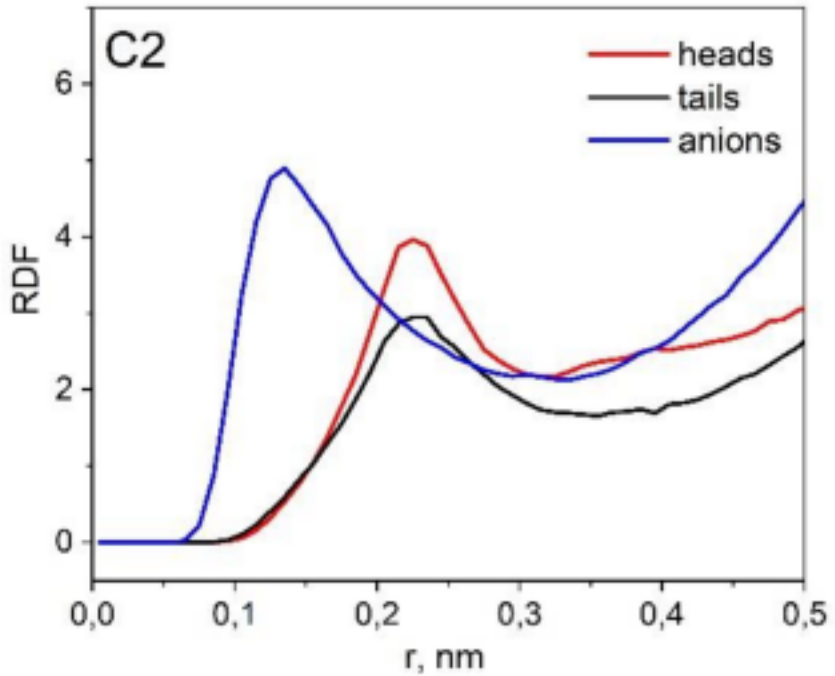
Distributions of the interstitial spheres radii

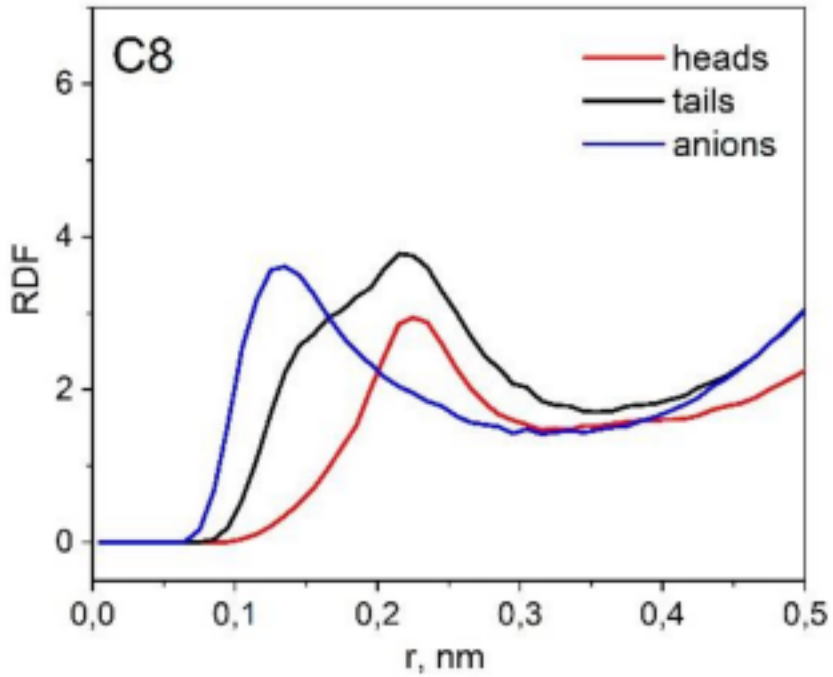


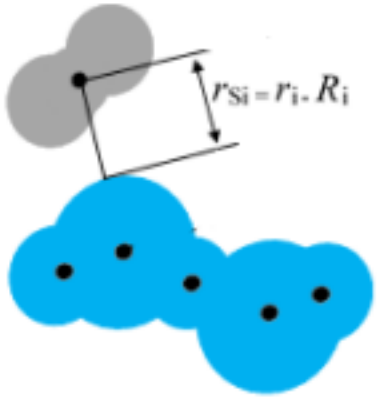
Interstitial spheres

Large interstitial spheres appear near the dissolved gas molecules. Additional empty volume is localized exclusively in their nearest environment.

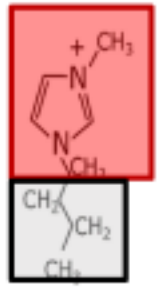
Where is CO_2 located? Radial Distribution Functions

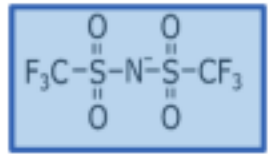






«heads»





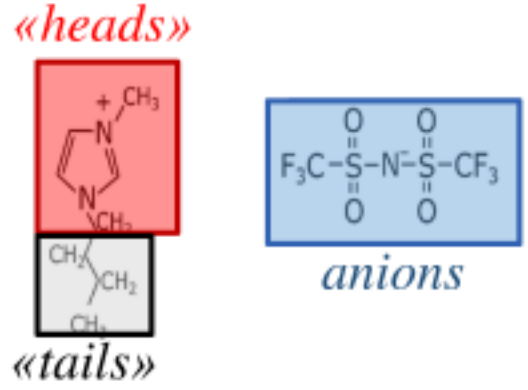
anions

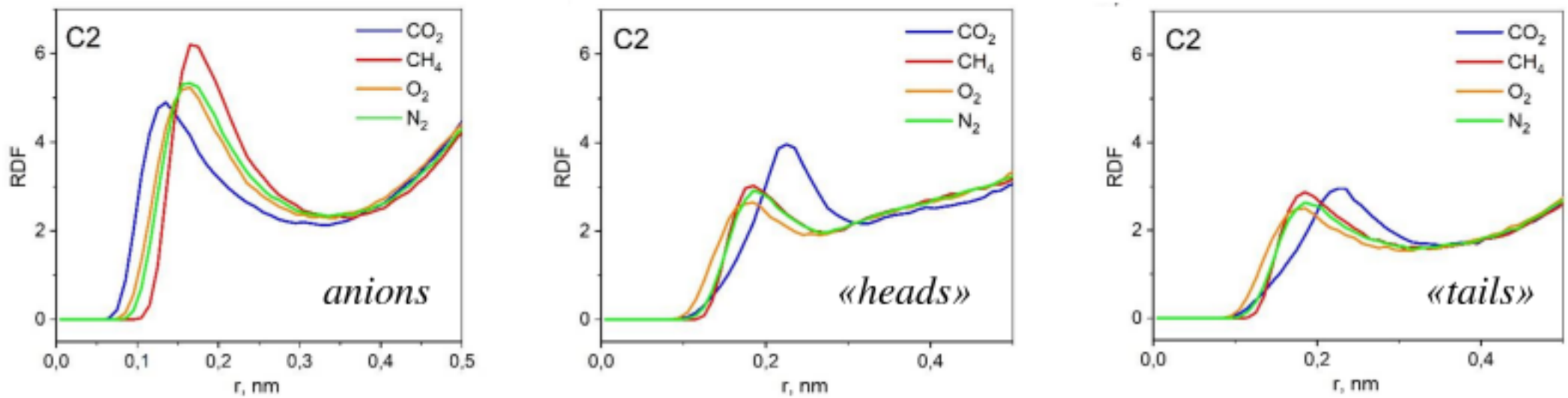
«tails»

RDF of dissolved CO_2 molecules relatively to the surfaces of anions (blue line), cation heads (red), and cation tails (black) in $[C_2MIM][NTf_2]$ and $[C_8MIM][NTf_2]$.

CO_2 molecules are located closer to the surfaces of anions than to the surfaces of the cations.

How is CO_2 arranged in comparison with other gases?

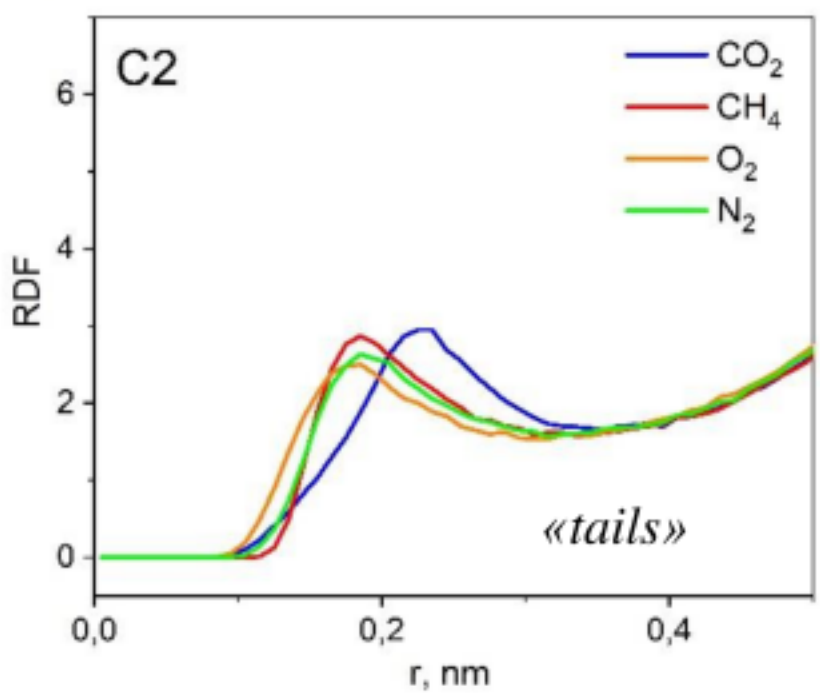


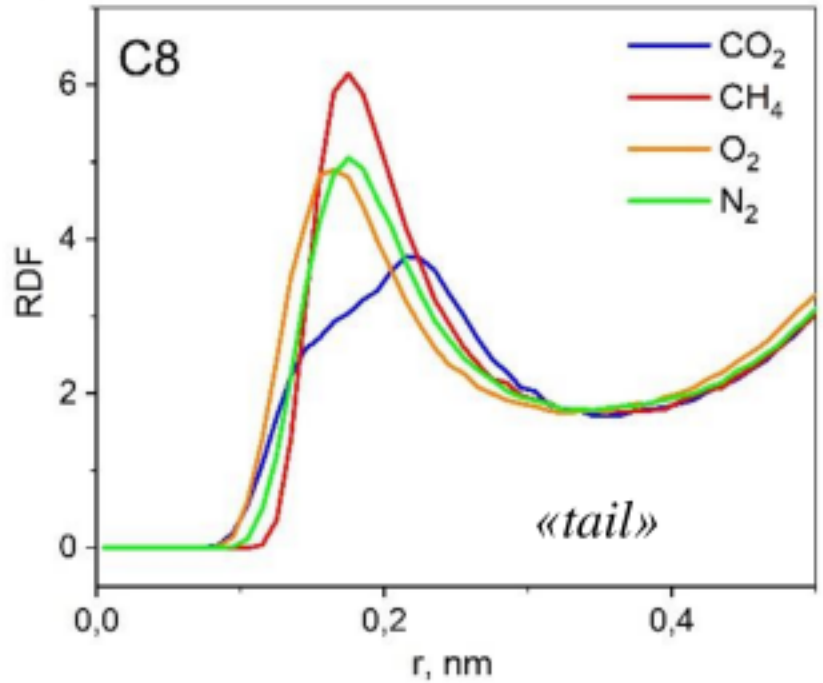


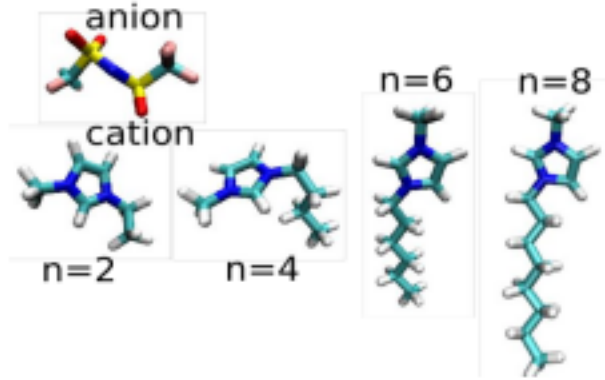
RDFs between gas centers and the surfaces of anions and cations.

CO_2 is located closer to anions than other gases and farther from the cations.

Dependence on the length of the alkyl substituent of the cation





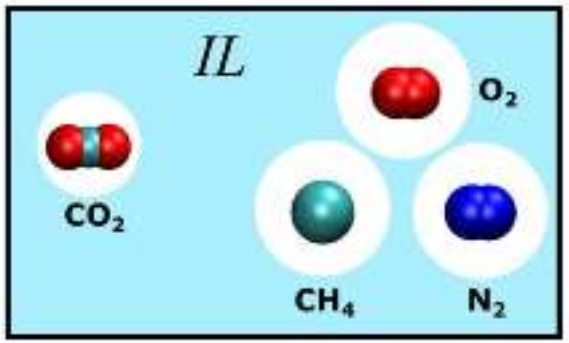


RDF between gas centers and the surfaces of cation tails in [C_2MIM][NTf_2] and [C_8MIM][NTf_2] ILs.

With an increase in the length of the alkyl substituent, the amount of CO_2 molecules near its surface also grows. However, CO_2 molecules distance themselves from cations, while all other gas molecules tend to be closer to them.

Conclusion

- CO_2, CH_4, O_2, N_2 introduce additional empty volume into the IL, locally loosening it.
- CO_2 molecules add a significantly smaller empty volume than O_2, N_2, and CH_4 molecules. One can propose that the high solubility of CO_2 is associated with the fact that its placement in an IL and the creation of the corresponding cavity is more energetically favorable compared to other gases.



- CO_2 molecules are located closer to the anions, while the remaining gases are closer to the cations (both to the heads and to their tails).

Thank you for your attention!