Supplementary Materials

Molecular mechanism of water permeation in a helium impermeable graphene and graphene oxide membrane

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The charge and atom types for the small units which were replicated to get the oxidized sheet (13.5% ($C_{38}O_3(OH)_2$) 25% ($C_{38}O_4(OH)_2$) and 33% ($C_{38}O_5(OH)_6$)) were shown in figure S1, S2 and S3. The initial configurations of the system for an oxidized graphene sheets in water and helium are shown in figure S4.

The PMF profiles of the other oxidised sheet (25% ($C_{38}O_4(OH)_2$)) in water and helium are given in S5. At this oxidation also the sheets in helium has only one global minimum, and for sheets in water, the free energy barrier between first layer of water and no layer is reduced compared to pristine sheets in water. This also suggests that the configurations with water in between the sheets are more accessible when the sheets are oxidised. There is a monotonic increase of depth of global min- ima (dgm) in helium case with oxidation: dgm(13.5%) $<$ dgm(25%) $<$ dgm(33%) with the exception of pristine case. This is because the interaction between the sheets in pristine case is vdW only, while for the oxidation cases it was vdW and electrostatic. The monotonic trend cannot be linear because the depth is also hugely dependent on relative placing of the functional groups on the sheets.

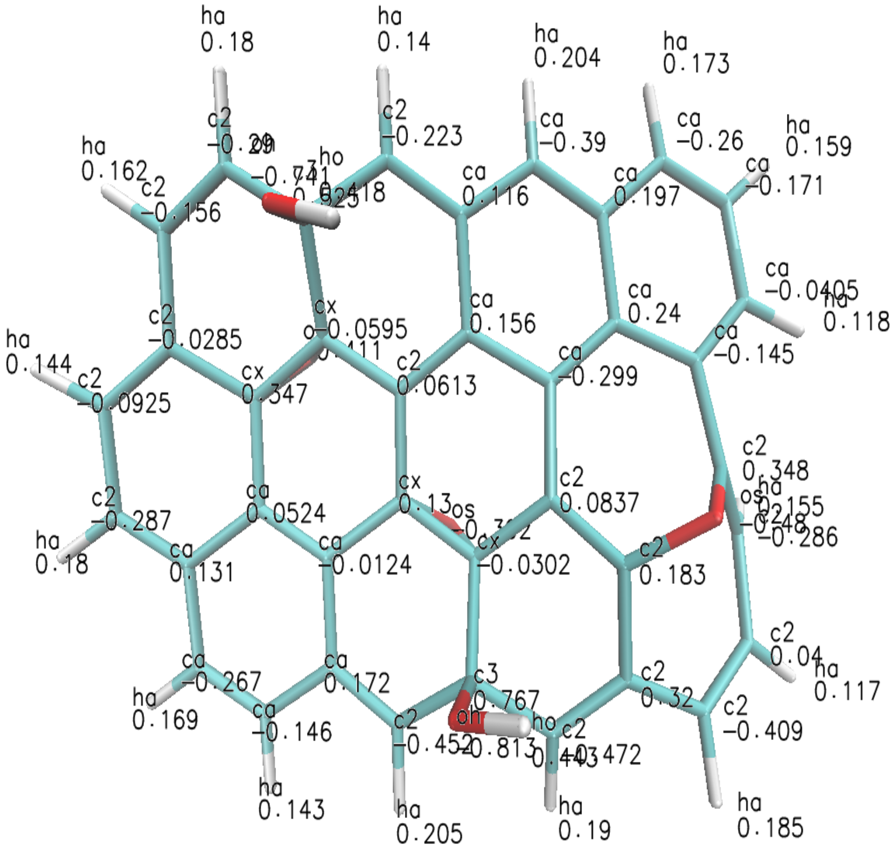

Figure S1 : The 13.5% oxidized graphene sheet flake which was used to make bigger sheets used in PMF calculations, showing the GAFF atom types and RESP charges.

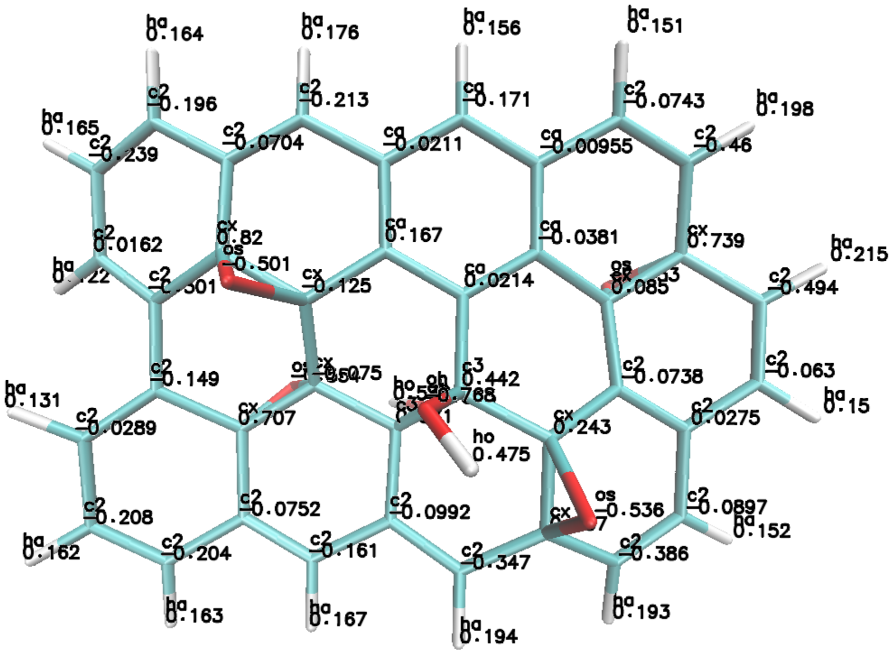

FIG. S2. The 25%($C_{38}O_4(OH)_2$) oxidized graphene sheet flake which was used to make bigger sheets used in PMF calculations, showing the GAFF atom types and RESP charges.

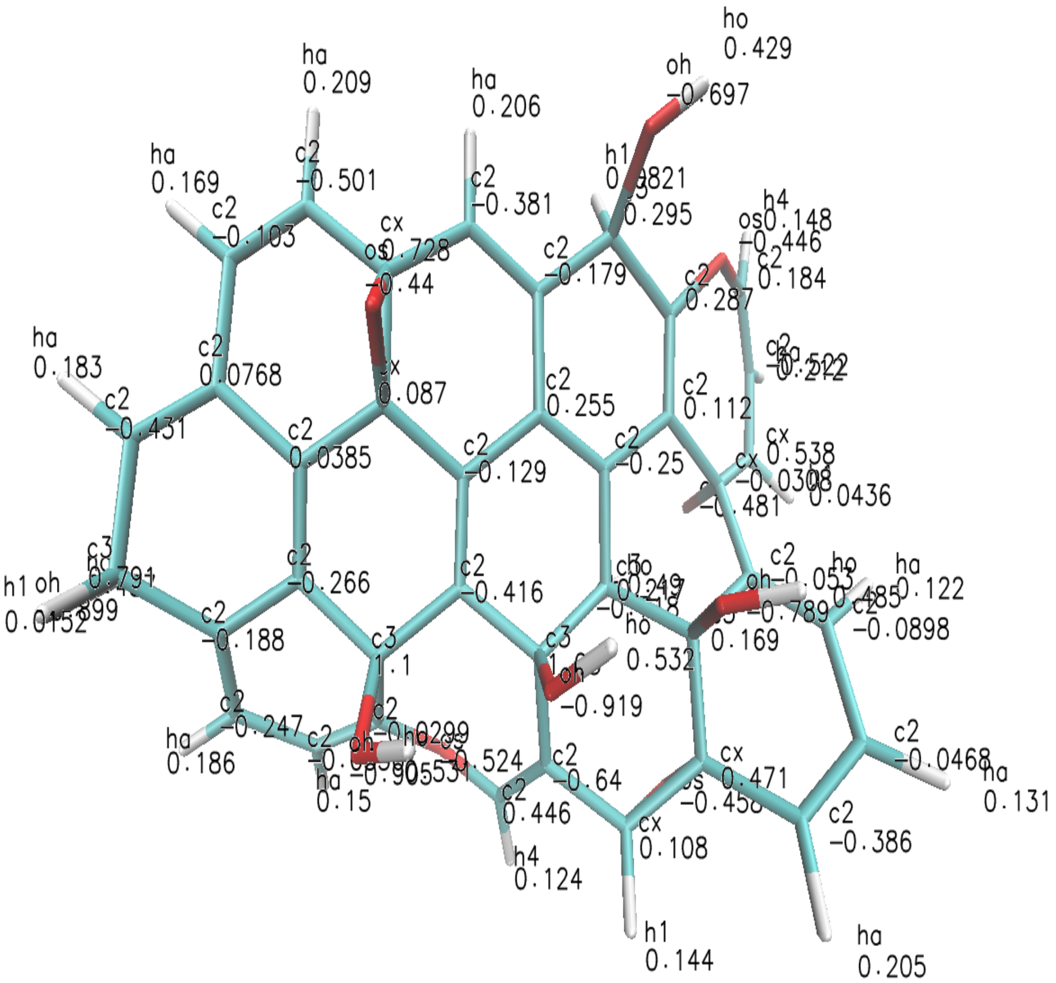

Figure S3 : The 33% oxidized graphene sheet flake which was to make bigger sheets used in PMF calculations, showing the GAFF atom types and RESP charges.

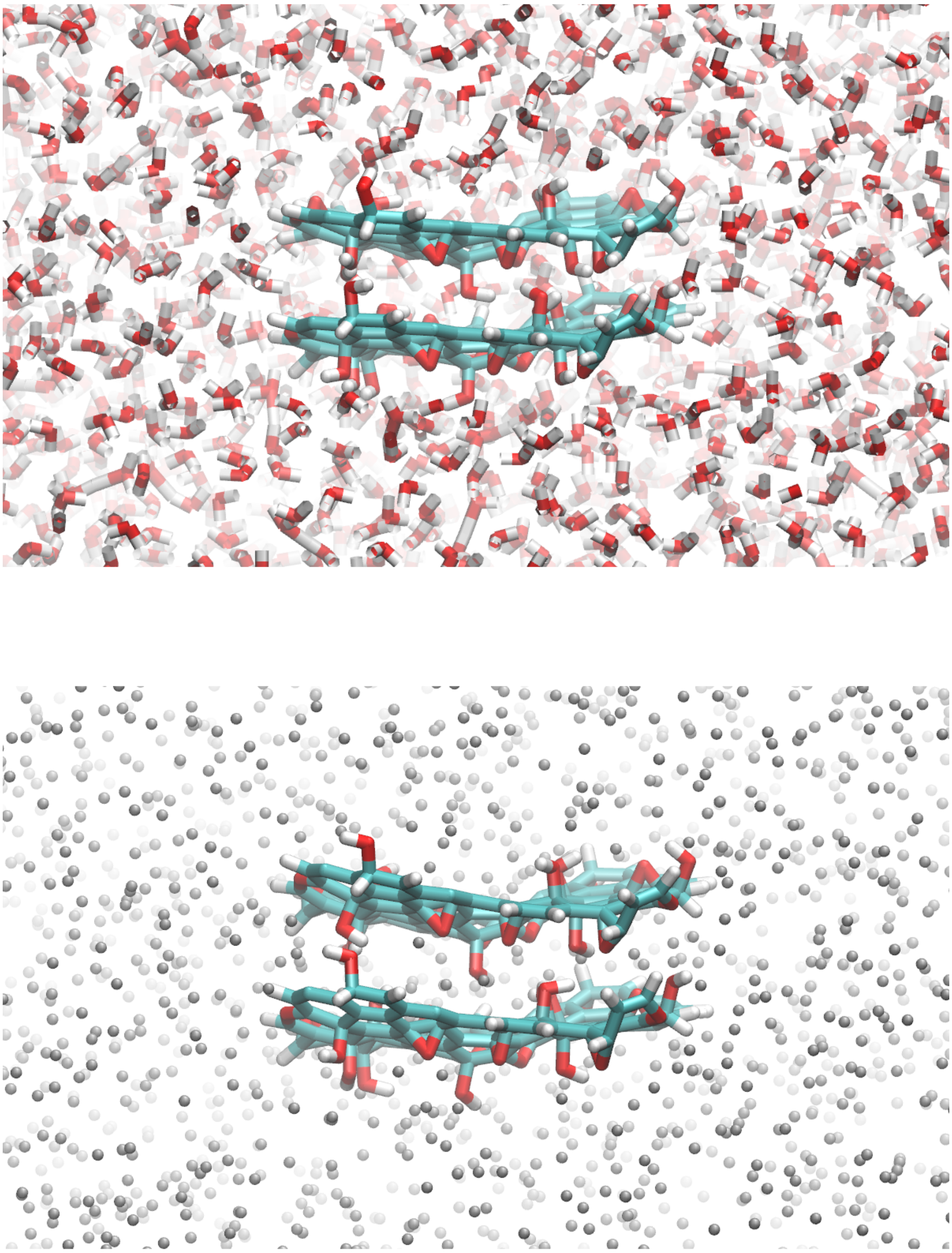

FIG. S4. The initial configuration of oxidized graphene sheets solvated in water (top) and helium (bottom). All other oxidized and pristine sheets were solvated similarly. For PMF calculations the sheets are pulled apart from the initial configuration.

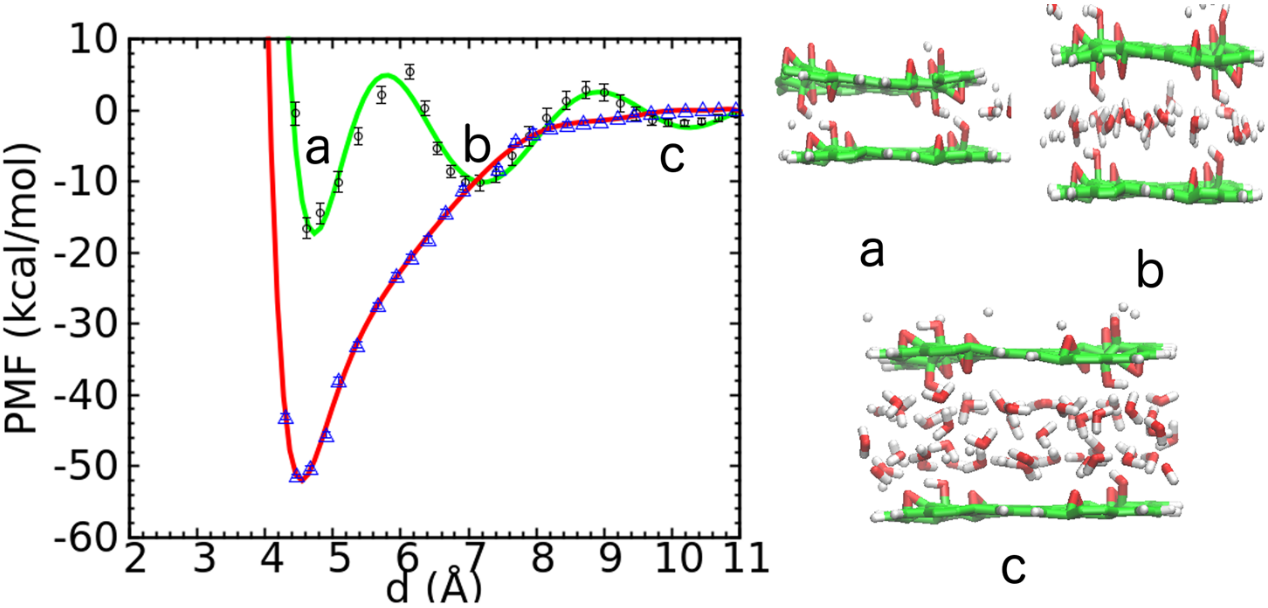

FIG. S5. PMF of functionalized graphene (25% oxidation) in water (black circles) and helium (blue triangles). The configurations at global 4.8 Å (a) and 7 Å(b) and local minimum 10 Å(c) in water are shown on the side. Polynomial fit to the PMF profile is a guide to the eye only.

We also present the average number of hydrogen bonds per water molecule trapped between oxidized graphene sheets and of water trapped between pristine graphene sheets at different separations in Table S1. We use the hydrogen bond criterion as O-O distance less than 3.5Å and O-O-H angle less than 30^o. We can see that at every corresponding separation the average number of hydrogen bonds of a water molecule are higher in the case of graphene. This is due to the superior sheet water interaction in the case of oxidized sheet that pulls water layers slightly apart.

TABLE S1. Table showing the rotational and translational entropies and diffusion coefficient and average number of hydrogen bonds of a water molecule trapped between reduced parts of graphene sheets at different separation

Separation(Å)	TS_{rot}(kcal/mol)	TS_{trans}(kcal/mol)	Diffusion Coefficient[a]	Hydrogen bond
6.5	3.30 ± 0.03	1.14 ± 0.01	1.02 ± 0.13	2.85 ± 0.01
8	3.89 ± 0.01	1.14 ± 0.01	2.43 ± 0.27	2.63 ± 0.03
9	3.73 ± 0.04	1.05 ± 0.02	3.17 ± 0.39	2.73 ± 0.02
10	3.71 ± 0.03	1.01 ± 0.01	2.33 ± 0.29	2.86 ± 0.01
12	3.82 ± 0.03	1.01 ± 0.03	2.97 ± 0.15	2.78 ± 0.01
15	3.87 ± 0.03	0.98 ± 0.01	3.50 ± 0.37	2.80 ± 0.01
bulk	4.03 ± 0.01	0.95 ±0.01	6.22 ± 0.90	2.55 ± 0.04

[a] in $\times 10^{-5}$cm^2/s

TABLE S2. Table showing the rotational and translational entropies and diffusion coefficient and average number of hydrogen bonds of a water molecule trapped between oxidized parts of graphene sheets at different separation

Separation (Å)	TS_{rot}(kcal/mol)	TS_{trans}(kcal/mol)	Diffusion Coefficient[a]	Hydrogen bond
7	2.83 ± 0.02	0.92 ± 0.01	0.16 ± 0.03	2.73 ± 0.09
8	3.00 ± 0.01	0.86 ± 0.01	0.38 ± 0.06	2.55 ± 0.03
9	3.04 ± 0.02	0.88 ± 0.01	0.47 ± 0.04	2.44 ± 0.04
10	3.20 ± 0.01	0.91 ± 0.01	0.73 ± 0.03	2.53 ± 0.03
12	3.38 ± 0.03	0.90 ± 0.01	1.23 ± 0.01	2.46 ± 0.02
15	3.52 ± 0.01	0.92 ± 0.01	1.91 ± 0.12	2.50 ± 0.01
bulk	4.03 ± 0.01	0.95 ±0.01	6.22 ± 0.90	2.55 ± 0.04

[a] in $\times 10^{-5}$cm^2/s

We also present the radial distribution of the oxygens of water. In the graphene case for separation 7 Å and 8 Å. They corroborate the hydrogen bond analysis, where the first peak is taller compared to oxidized sheet case. Both the cases exhibit ordering compared to the bulk case. In the case of oxidized sheet the first peak in bulk and at separations 7 Å and 8 Å as seen in figure S7 are of similar height, indicating the similarity of bulk and one layer environment between oxidized sheets. The single layer of water trapped between oxidized sheets (figure S7) at 7 Å shows improved ordering (prominent second peak) compared to bulk just like in the case of pristine sheet (figure S6).

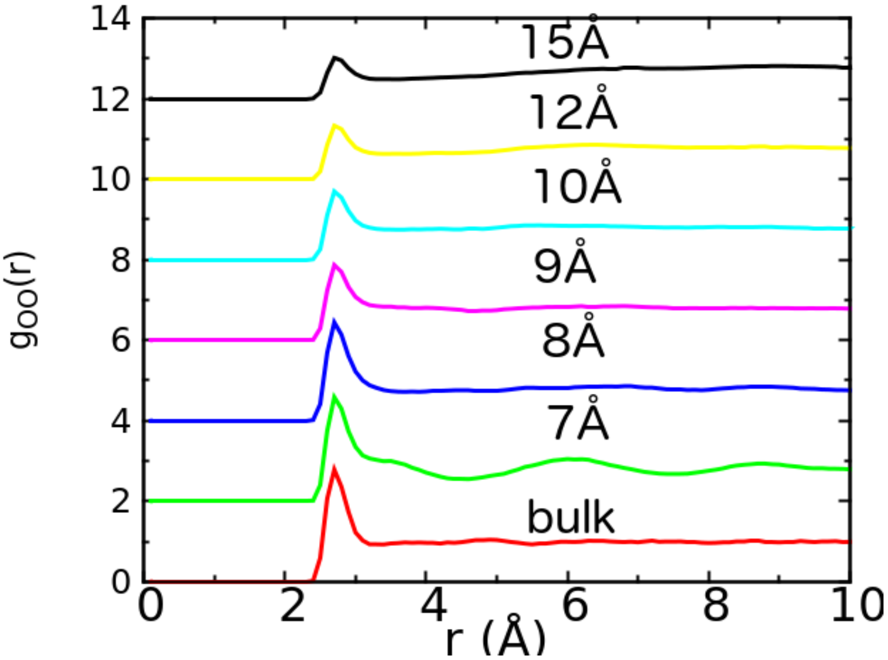

Figure S6 : Radial distribution function of oxygens in water, trapped between oxidized graphene sheets. From bottom to top, bulk (red), at a separation of sheets of 7Å (green), 8Å (blue), 9Å (pink), 10Å (light blue) 12Å (yellow). The profiles have been shifted 2Å on the y-axis for clarity.

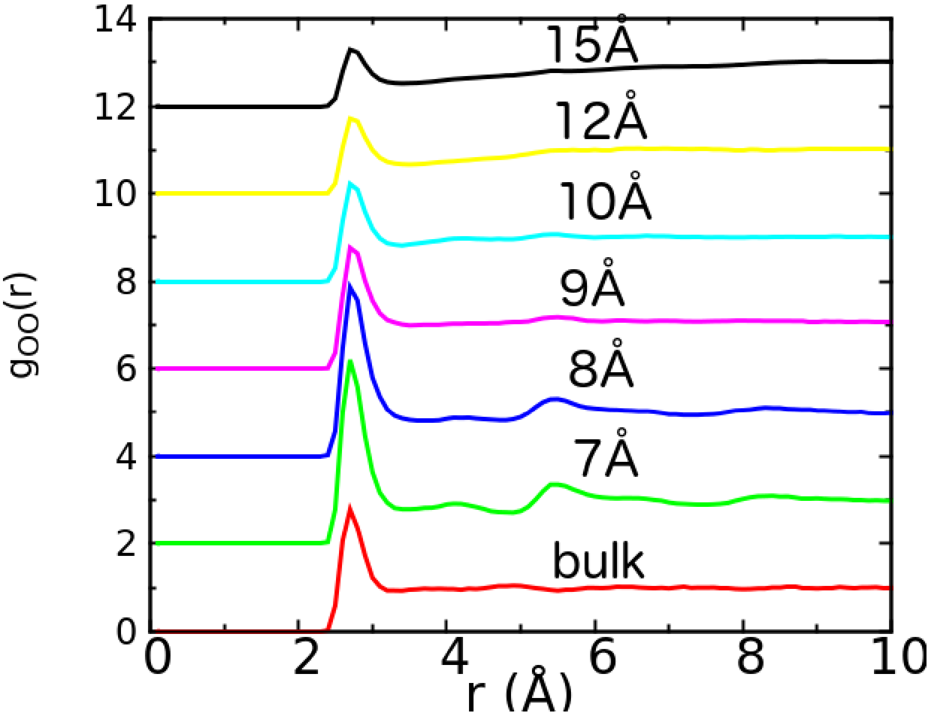

Figure S7: Radial distribution function of oxygens in water, trapped between pristine graphene sheets. From bottom to top, bulk (red), at a separation of sheets of 7Å (green), 8Å (blue), 9Å (pink), 10Å (light blue) 12Å (yellow). The profiles have been shifted 2Å on the y-axis for clarity.