

Adsorption of 5-fluorouracil, an anticancer drug, in faujasite-type zeolites: Understanding storage and release with density functional theory calculations

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SUPPORTING INFORMATION

S1.1 – Monte Carlo simulations

S1.2 – Simulated annealing

S1.3 – Force field parameters

S1.4 – Calculation of internal energy of adsorption

S2.1 – Adsorption energies of individual configurations

S2.2 – Internal energies of adsorption

S2.3 – Visualisation of additional low-energy configurations

S2.4 – RDFs obtained from AIMD simulations of 5-FU@FAU

S2.5 – Partial charges of 5-FU

S2.6 – Intramolecular bond distances and vibrational modes

S2.7 – Initial structures used in AIMD simulations of (5-FU+16H₂O)@FAU

S2.8 – RDFs obtained from AIMD simulations of (5-FU+16H₂O)@FAU

S2.9 – RDFs obtained from AIMD simulations of 5-FU in water

References

S1.1 – Monte Carlo simulations

The Monte Carlo simulations were carried out using the *Sorption* module included in *Materials Studio* (DS BIOVIA). To generate starting configurations of 5-FU in different zeolite models, fixed-loading simulations (*NVT* ensemble) were performed for a loading of one 5-FU molecule per unit cell. Relevant simulation settings (except force field parameters, which are discussed in S1.3) are compiled in **Table S1**.

Table S1: Overview of settings used in fixed-loading MC simulations

Loading	1 5-FU per cell
Temperature	298 K
Sampling method	Metropolis
# equilibration steps	500,000
# production steps	2,000,000
Step probability	Exchange:Translation:Rotation:Regrowth: 2:1:1:0.1
Electrostatic interactions	Ewald & Group summation Ewald accuracy: 0.001 kcal/mol Cutoff: 12.5 Å
Van der Waals interactions	Atom-based summation Cutoff: 12.5 Å Spline-based truncation, cubic spline width 1 Å

Five independent MC simulations were run for each adsorbent model. 20 low-energy configurations and 20 additional snapshots were extracted from the production stage of each simulation. The 5-FU positions of all configurations were optimised using the *Forcite* module of *Materials Studio*, employing “ultra-fine” optimisation settings. Between 3 and 10 distinct configurations were then selected as input for the DFT optimisations. In the labels of the configurations used in **Table S4**, which are of the kind ConfigX (with X = 1, 2...), the ordering follows the adsorption energy obtained from the FF-based optimisations.

S1.2 – Simulated annealing

To study the co-adsorption of water, 16 H₂O molecules were added to pre-optimised low-energy 5-FU@FAU models. These simulations employed the *Adsorption Locator* module of *Materials Studio*. This module uses a simulated annealing procedure based on a series of MC simulations during which the temperature is decreased from a very high starting value to low temperature in order to probe different local minima. Each simulated annealing run consisted of 20 cycles, with 100,000 simulation steps per cycle. During each cycle, the temperature was gradually decreased from 100,000 to 100 K. Force field parameters and other settings were largely analogous to those reported above for the MC simulations. To ensure that the H₂O molecules are adsorbed in the vicinity of the 5-FU molecule, additional constraints fixing the “adsorption distance” (maximal distance between 5-FU and each adsorbed H₂O molecule) to 6 Å were enforced. At least three independent simulated annealing runs were performed for each adsorbent model of interest. At the end of each annealing cycle, the positions of the H₂O molecules were optimised, using parameters and settings as described above for the MC simulations. Out of the at least 60 configurations generated in this way, low-energy configurations were selected as starting point for the AIMD simulations (**Figure S7 to S9**).

S1.3 – Force field parameters

5-FU and H₂O molecules were represented using default parameters from the PCFF force field that are distributed with *Materials Studio* (Table S3).¹ PCFF uses 9-6 Lennard-Jones (LJ) potentials and a 6th-power combination rule.² Regarding the zeolite frameworks, partial charges and LJ parameters proposed by Emami et al. were employed for Si atoms and O atoms of Si–O–Si linkages.³ In the view of the identical number of electrons of Si⁴⁺ and Al³⁺ cations, the LJ parameters of Si were also used for framework Al atoms. LJ parameters originally proposed for O_{Si–O–Si} atoms were also used for O_{Si–O–Al} atoms, and LJ parameters for hydrogen atoms of silanol groups derived in the work of Emami et al. were assigned to the framework protons.

While it seems plausible to assume that the LJ parameters are not heavily affected by moderate differences in the atomic environment, new partial charges had to be derived for those species present in aluminosilicate zeolites that were not covered in the study of Emami et al., specifically, framework protons, Al atoms, and oxygen atoms of AlO₄ tetrahedra. For this purpose, the following stepwise approach was used:

- A DFT single-point calculation for the GULP-optimised structure of H-FAU_1H was performed using the *CP2K* code, employing settings analogous to those described in the main manuscript. The calculation of charges based on the electrostatic potential in the framework of the REPEAT method⁴ was activated with the flag &USE_REPEAT_METHOD in the block &FORCE_EVAL &PROPERTIES &RESP of the *CP2K* input.
- In order to ensure that the same charges are assigned to atoms with an identical environment, EQUAL_CHARGES constraints were enforced for a) all Si atoms, b) O atoms of Si–O–Si links, c) O atoms of unprotonated Si–O–Al links.
- The REPEAT calculation resulted in $q(\text{Si}) = 0.826 e$ and $q(\text{O}_{\text{Si–O–Si}}) = -0.413 e$. Since the charge values of these atom types should correspond to those proposed by Emami et al. ($q(\text{Si}) = 1.10 e$ and $q(\text{O}_{\text{Si–O–Si}}) = -0.55 e$), a scaling factor of $1.10/0.826 \approx 1.332$ was used to rescale the REPEAT charges for all species (q_{scaled}). Finally, the charges of some atoms were slightly adjusted (in the 2nd or 3rd digit) to result in overall charge neutrality (q_{adjusted}). Table S2 provides REPEAT charges, scaled charges, and adjusted charges for the zeolite framework atoms.

Table S2: Results of charge derivation procedure based on REPEAT calculations.

Species	q_{REPEAT} [e]	q_{scaled} [e]	q_{adjusted} [e]
Si	0.826	1.100	1.100
Al	0.853	1.136	1.130
O _{Si–O–Si}	-0.413	-0.550	-0.550
O _{Si–O–Al} (not protonated)	-0.533	-0.710	-0.720
O _{Si–O–Al} (protonated)	-0.387	-0.515	-0.510
H	0.332	0.442	0.440

Table S3: Atom types and non-bonded PCFF parameters used in force field calculations. 5-FU atom labels correspond to those shown in **Figure 1** of the main paper. Partial charges q and Lennard-Jones parameters R_0 and D_0 are given for each atom. NI (no interaction) indicates that only a partial charge, but no LJ potentials were assigned to this atom.

5-FU molecule	Atom type (PCFF)	q [e]	R_0 [Å]	D_0 [kcal mol ⁻¹]
C2	c_2	0.807	3.81	0.120
C4	c_1	0.642	3.81	0.120
C5	c=1	0.130	4.01	0.064
C6	c=	-0.0268	3.90	0.064
N1	n_2	-0.589	3.60	0.106
N3	n_2	-0.600	3.60	0.106
O2	o_1	-0.585	3.30	0.267
O4	o_1	-0.531	3.30	0.267
F	f	-0.130	3.20	0.0598
H1, H3	hn2	0.378	1.65	0.013
H6	hc	0.1268	NI	NI
H₂O molecule				
O	o*	-0.7982	3.608	0.274
H	hw	0.3991	1.098	0.013
Zeolite				
Si	sz	1.100	4.20	0.080
Al	az	1.130	4.20	0.080
O _{Si-O-Si}	oss	-0.550	3.60	0.040
O _{Si-O-Al} (not protonated)	oas	-0.720	3.60	0.040
O _{Si-O-Al} (protonated)	ob	-0.510	3.60	0.040
H	hb	0.440	1.098	0.013

S1.4 – Calculation of internal energy of adsorption

For adsorption of 5-FU in a given FAU model, the internal energy of adsorption was computed as:

$$\Delta U_{ads} = \langle \bar{E}_{5FU@FAU} \rangle_{3tr} - \langle \bar{E}_{FAU} \rangle_{3tr} - \langle \bar{E}_{5FU} \rangle_{3t}$$

Here, the terms in brackets correspond to the averages over the total energies (sum of potential and kinetic energy) obtained from the production stages of the AIMD simulations ($T = 298$ K) for the 5-FU@FAU model, the guest-free zeolite, and for 5-FU in a box. The index “3tr” highlights that these averages were computed over the three independent trajectories (4 trajectories were computed for 5-FU@SiO₂-FAU, see main text). In order to estimate error bars for the internal energies of adsorption, ΔU_{ads} values were recomputed using only 2 trajectories for each system, considering all possible permutations. Of these, the combination resulting in the most negative internal energy of adsorption (*i.e.*, most negative $\langle \bar{E}_{5FU@FAU} \rangle_{2tr}$, least negative $\langle \bar{E}_{FAU} \rangle_{2tr}$ and $\langle \bar{E}_{5FU} \rangle_{2tr}$) was taken as upper boundary value $\Delta U_{ads,max}$ and the one giving the least negative internal energy of adsorption (*i.e.*, least negative $\langle \bar{E}_{5FU@FAU} \rangle_{2tr}$, most negative $\langle \bar{E}_{FAU} \rangle_{2tr}$ and $\langle \bar{E}_{5FU} \rangle_{2tr}$) was taken as lower boundary value $\Delta U_{ads,min}$.

S2.1 – Adsorption energies of individual configurations

Table S4: DFT adsorption energies computed for individual configurations with DZVP and TZVP basis sets. For each FAU model, the lowest-energy configuration according to TZVP calculations is highlighted in bold. The last column lists hydrogen bonds (having bond distances ≤ 2.5 Å) and, where applicable, the occurrence of framework deprotonation.

5FU@...	ΔE_{ads} (DZVP) [kJ mol ⁻¹]	ΔE_{ads} (TZVP) [kJ mol ⁻¹]	Comments
SiO₂-FAU			
Config1	-84.9	-72.8	No H-bond
Config2	-83.3	-73.2	H-bond: H1...O _{fw}
Config3	-80.9	-66.7	No H-bond
Config4	-71.3	-64.6	H-bond: H3...O _{fw}
Config5	-67.0	-60.4	H-bond: H3...O _{fw}
Config6	-68.4	-60.7	H-bond: H3...O _{fw}
H-FAU_1H			
Config1	-154.9	-134.4	Deprotonation: H _{fw} @O2; H-bond: H3...O _{fw}
Config2	-164.5	-144.0	Deprotonation: H _{fw} @O4; H-bond: H3...O _{fw}
Config3	-131.8	-121.7	H-bonds: H _{fw} ...O2, H3...O _{fw}
Config4	-143.1	-127.6	H-bond: H _{fw} ...O2
Config5	-158.3	-131.3	Deprotonation: H _{fw} @O2
Config6	-127.3	-110.9	H-bonds: H _{fw} ...O4, H3...O _{fw}
H-FAU_2H_1_3			
Config1	-196.0	-179.2	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config2	-185.1	-165.8	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config3	-169.9	-154.5	Deprotonation: H _{fw} @O4; H-bonds: H1...O _{fw} , H3...O _{fw}
H-FAU_2H_1_4			
Config1	-206.3	-188.7	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config2	-205.9	-188.9	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config3	-185.4	-168.0	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
H-FAU_3H			
Config1	-188.8	-171.8	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config2	-165.9	-152.4	H-bonds: H _{fw} ...O2, H _{fw} ...O4
Config3	-192.8	-173.9	H-bonds: H _{fw} ...O2, H _{fw} ...O4
Config4	-172.6	-158.8	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config5	-193.2	-177.3	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H1...O _{fw}
Config6	-175.0	-153.4	H-bonds: H _{fw} ...O2, H _{fw} ...O4
Config7	-188.8	-162.3	H-bonds: H _{fw} ...O2, H _{fw} ...O4
Config8	-168.8	-153.1	H-bonds: H _{fw} ...O2, H _{fw} ...O4, H3...O _{fw}

H-FAU_16H			
Config1	-155.9	-142.1	H-bonds: H _{fw} ···O2, H3···O _{fw}
Config2	-157.6	-144.2	H-bonds: H _{fw} ···O4, H1···O _{fw} , H3···O _{fw}
Config3	-147.0	-135.5	H-bonds: H _{fw} ···O2, H3···O _{fw}
Config4*	-158.6	-143.2	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H3···O _{fw}
Config5	-160.3	-142.5	H-bonds: H _{fw} ···O4, H3···O _{fw}
Config6	-165.3	-148.3	Deprotonation: H _{fw} @O2; H-bond: H3···O _{fw}
Config7	-136.8	-126.6	H-bonds: H _{fw} ···O4, H1···O _{fw}
H-FAU_32H_1_3			
Config1	-198.5	-183.8	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config2	-188.1	-175.0	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config3	-193.1	-177.6	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config4	-197.2	-184.3	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw} , H6···O _{fw}
Config5	-195.9	-180.8	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config6	-188.9	-172.3	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config7	-192.6	-169.4	H-bonds: H _{fw} ···O2, H _{fw} ···O4
Config8*	-169.7	-151.4	H-bonds: H _{fw} ···O2, H _{fw} ···O4
Config9	-164.3	-154.6	H-bonds: H _{fw} ···O4, H3···O _{fw}
Config10	-165.5	-151.7	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H3···O _{fw}
H-FAU_32H_1_4			
Config1	-196.1	-178.4	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config2	-194.2	-182.1	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config3	-196.3	-180.9	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config4	-189.3	-174.2	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw} , H6···O _{fw}
Config5	-189.1	-173.9	H-bonds: H _{fw} ···O2, H _{fw} ···O4
Config6	-187.6	-174.2	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config7	-179.5	-166.6	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw} , H6···O _{fw}
Config8	-180.7	-163.8	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config9	-179.2	-164.3	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}
Config10	-180.3	-163.1	H-bonds: H _{fw} ···O2, H _{fw} ···O4, H1···O _{fw}

*Configuration with hydrogen bonds involving protons of neighbouring 12MRs

S2.2 – Internal energies of adsorption

Table S5: Internal energies of adsorption and upper and lower boundary values obtained from AIMD simulations.

	ΔU_{ads} [kJ mol ⁻¹]	$\Delta U_{ads,max}$ [kJ mol ⁻¹]	$\Delta U_{ads,min}$ [kJ mol ⁻¹]
SiO ₂ -FAU	-75.9	-86.5	-66.2
H-FAU_1H	-141.8	-148.4	-130.3
H-FAU_2H_1_3	-169.7	-178.6	-157.6
H-FAU_2H_1_4	-186.8	-208.8	-171.4
H-FAU_32H_1_3	-192.3	-198.3	-185.7

S2.3 – Visualisation of additional low-energy configurations

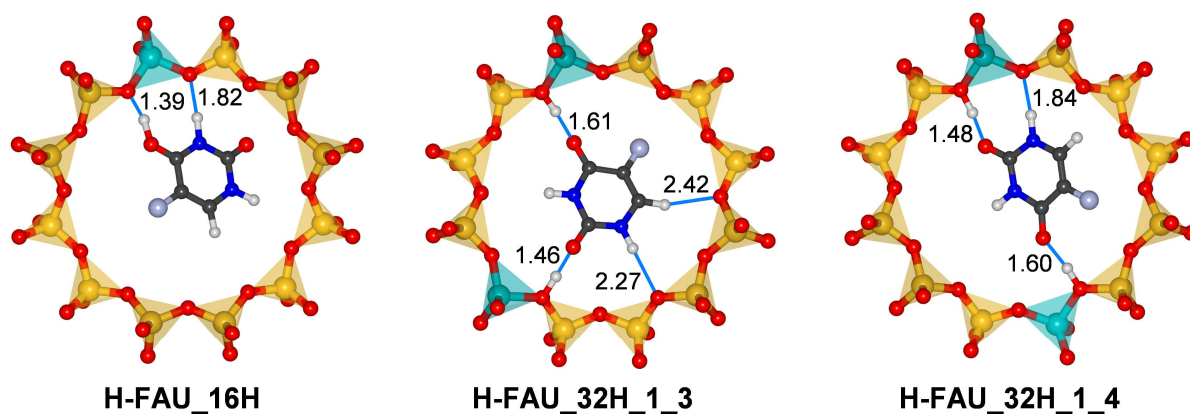


Figure S1: Lowest-energy configurations of 5-FU in additional FAU models not shown in **Figure 3**. Hydrogen bonds are displayed as blue lines, with distances given in Å.

S2.4 – RDFs obtained from AIMD simulations of 5-FU@FAU

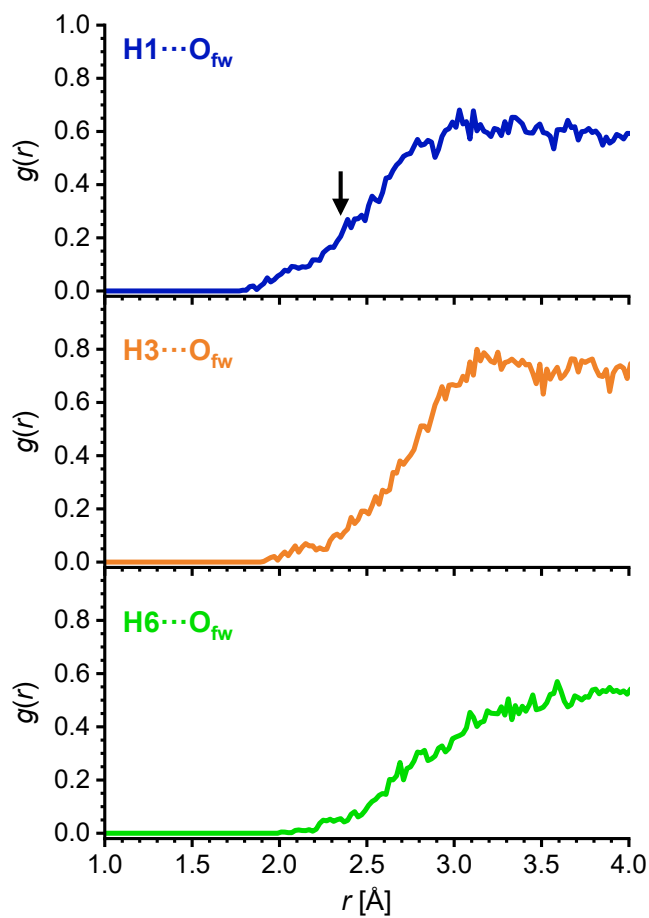


Figure S2: RDFs for selected combinations of atoms obtained from AIMD simulations of 5-FU@SiO₂-FAU. The black arrow indicates the hydrogen bond distance in the DFT-optimised structure shown in **Figure 3** (top row, central panel).

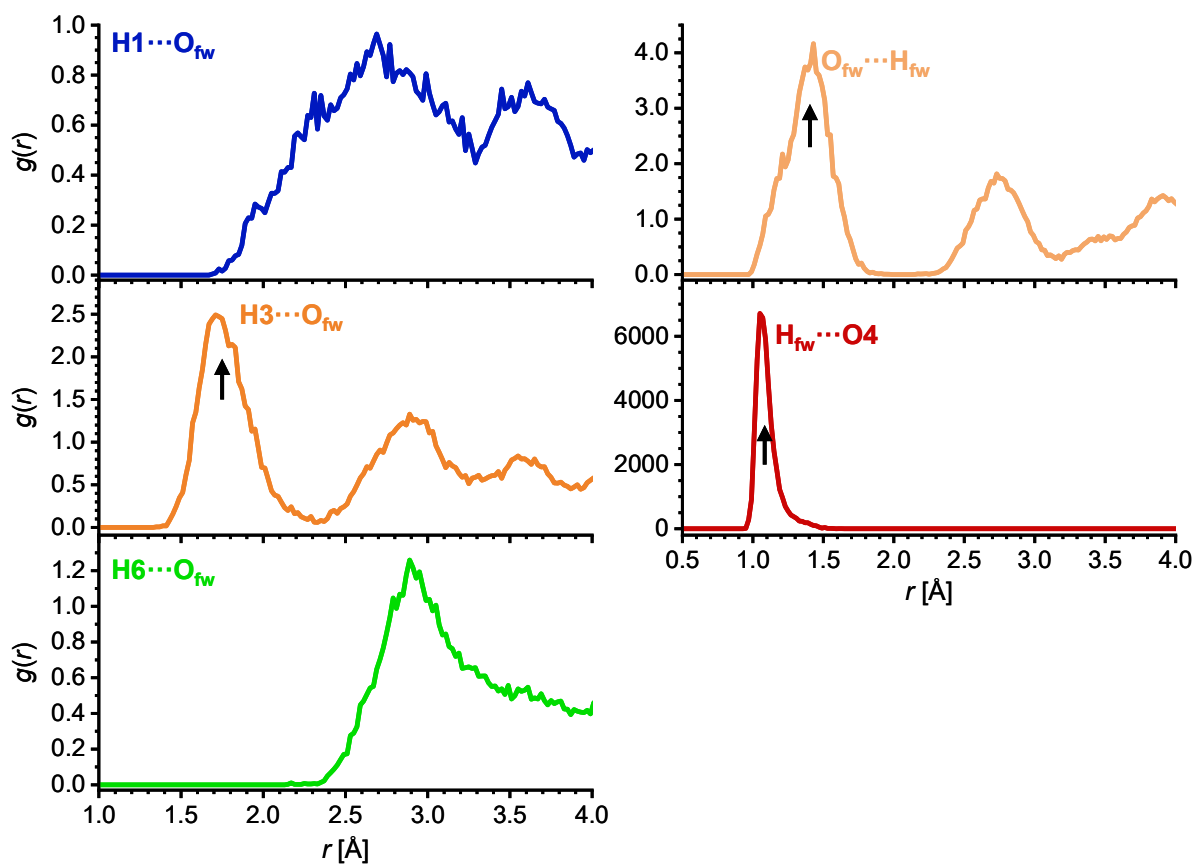


Figure S3: RDFs for selected combinations of atoms obtained from AIMD simulations of 5-FU@H-FAU_1H. The black arrows indicate distances in the DFT-optimised structure shown in **Figure 3** (top row, right panel).

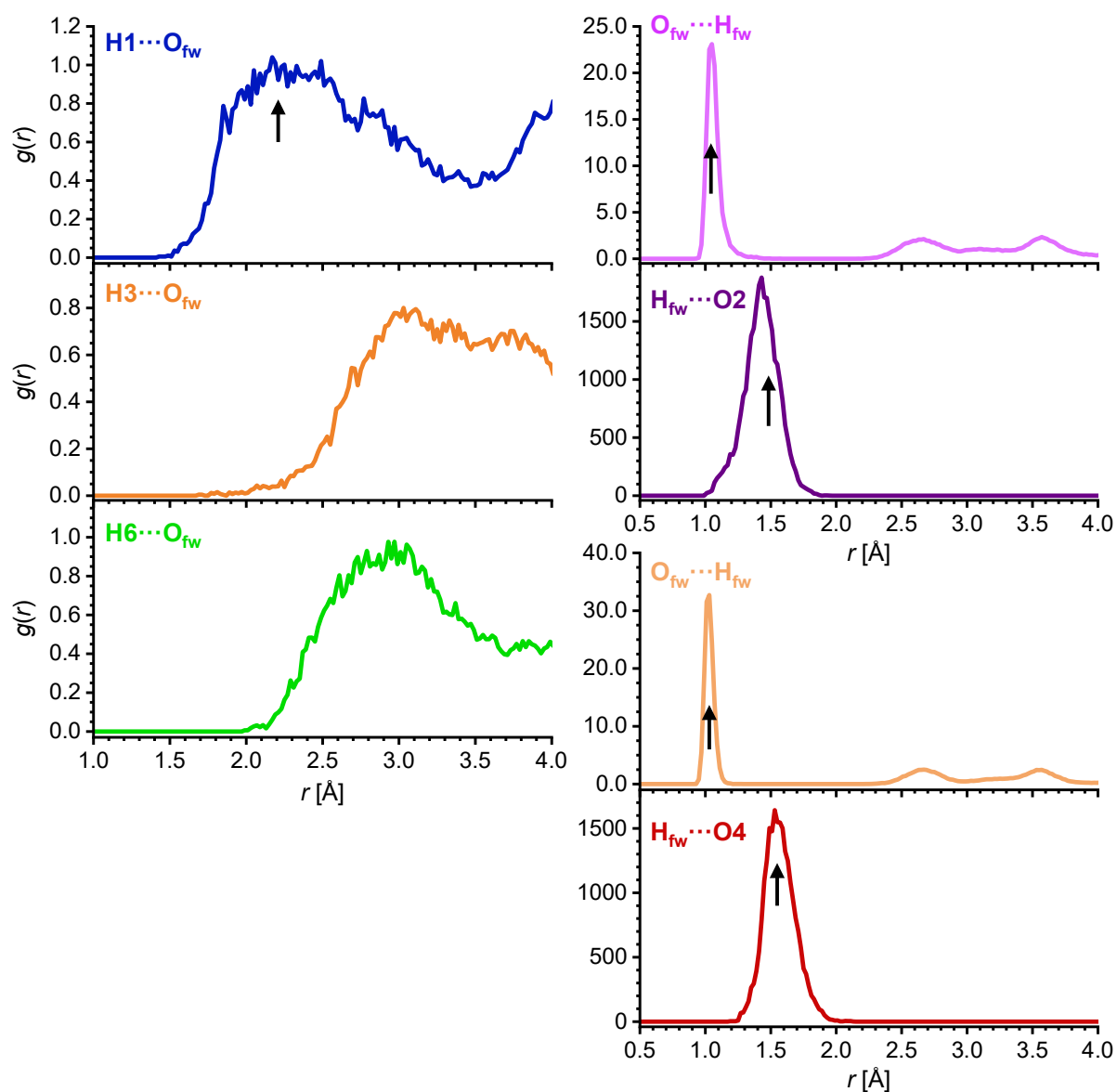


Figure S4: RDFs for selected combinations of atoms obtained from AIMD simulations of 5-FU@H-FAU_2H_1_3. The black arrows indicate distances in the DFT-optimised structure shown in **Figure 3** (bottom row, left panel).

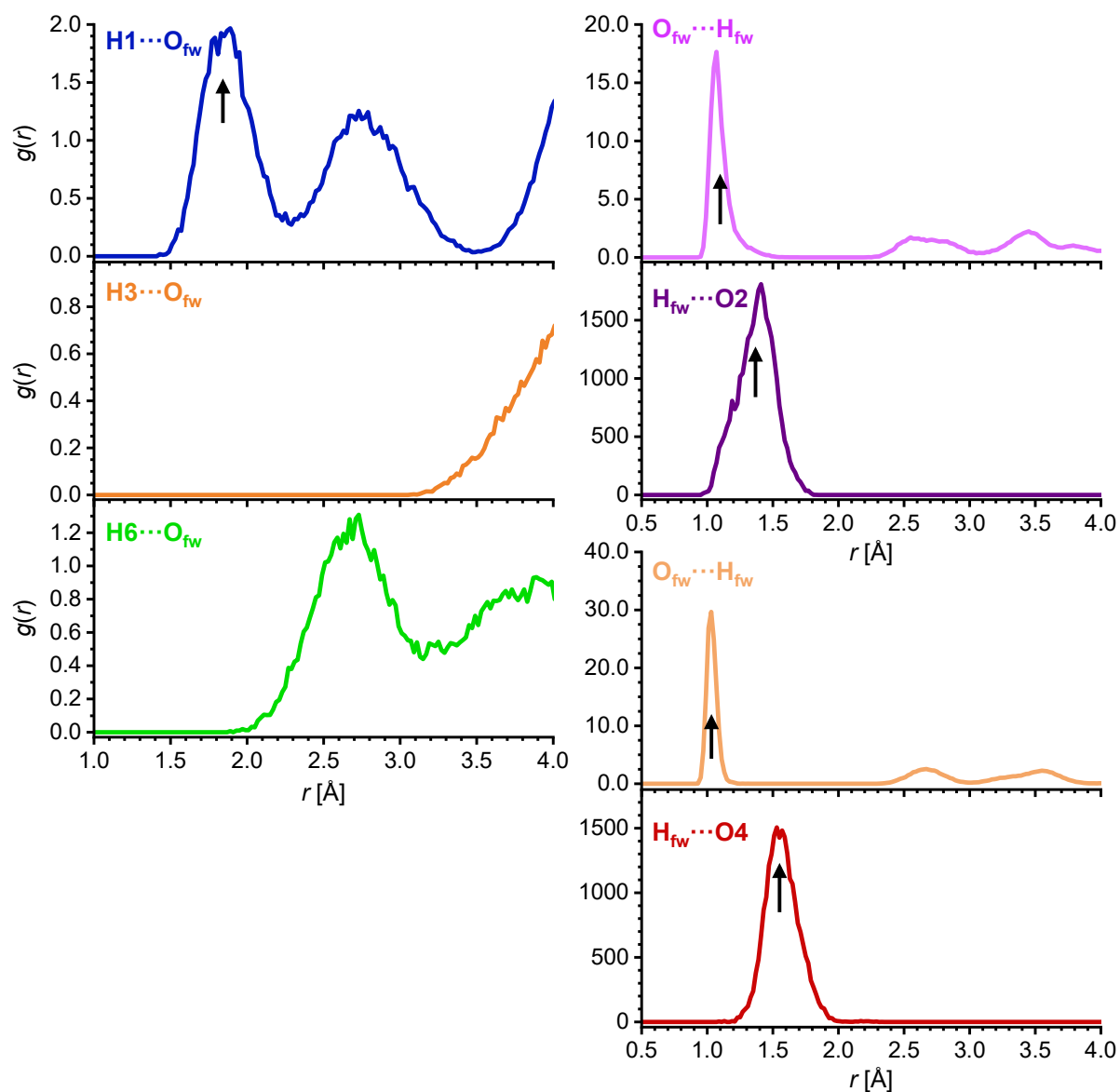


Figure S5: RDFs for selected combinations of atoms obtained from AIMD simulations of 5-FU@H-FAU_2H_1_4. The black arrows indicate distances in the DFT-optimised structure shown in **Figure 3** (bottom row, central panel).

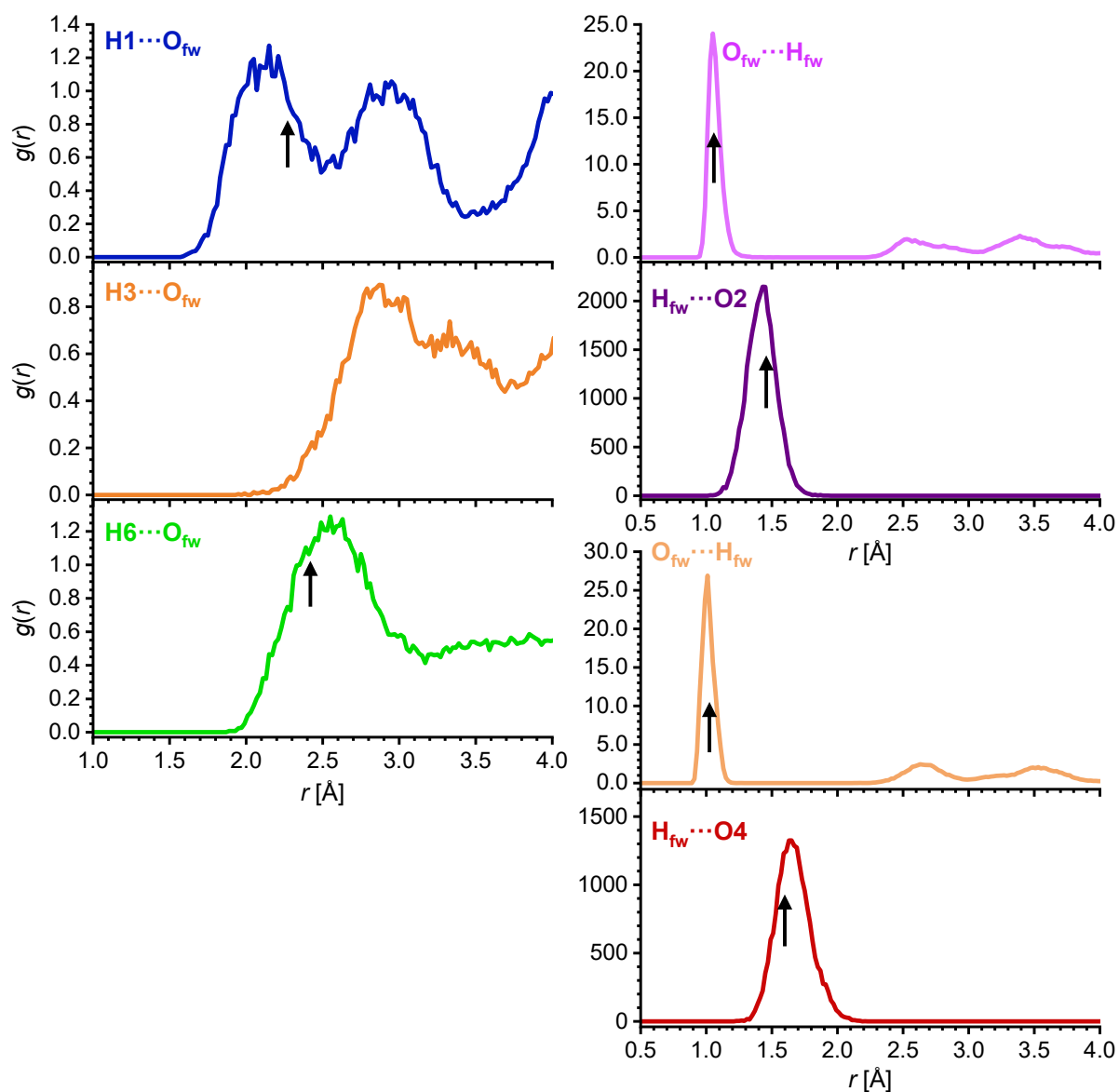


Figure S6: RDFs for selected combinations of atoms obtained from AIMD simulations of 5-FU@H-FAU_32H_1_3. The black arrows indicate distances in the DFT-optimised structure shown in **Figure S1** (central panel).

S2.5 – Partial charges of 5-FU

Table S6: DFT partial charges of the 5-FU molecule computed according to the Mulliken, Hirshfeld, and Restrained Electrostatic Potential (RESP) methods. Results obtained using the rev-vdW-DF2 functional and TZVP basis sets.

Atom	Mulliken charge [e]	Hirshfeld charge [e]	RESP charge [e]
N1	-0.011	-0.539	-0.081
H1	0.168	0.532	0.253
C2	0.145	0.481	0.184
O2	-0.294	-0.509	-0.426
N3	-0.049	-0.544	-0.009
H3	0.177	0.535	0.213
C4	0.140	0.393	0.233
O4	-0.276	-0.469	-0.414
C5	0.125	0.276	0.198
F	-0.196	-0.329	-0.168
C6	-0.023	-0.283	-0.138
H6	0.094	0.465	0.154

S2.6 – Intramolecular bond distances and vibrational modes

Table S7: Top: DFT-optimised Intramolecular bond distances of 5-FU and, where applicable, frequencies of stretching modes. **Bottom:** Frequencies of selected additional modes.

	Free 5-FU		5-FU@ SiO ₂ -FAU (Config2)		5-FU@ H-FAU_1H		5-FU@ H-FAU_2H_1_3	
	<i>d</i> [Å]	<i>v</i> [cm ⁻¹]	<i>d</i> [Å]	<i>v</i> [cm ⁻¹]	<i>d</i> [Å]	<i>v</i> [cm ⁻¹]	<i>d</i> [Å]	<i>v</i> [cm ⁻¹]
N1-C2	1.398		1.391		1.404		1.375	
C2-N3	1.395		1.394		1.415		1.387	
N3-C4	1.417		1.415		1.360		1.405	
C4-C5	1.458		1.453		1.428		1.448	
C5=C6	1.352	1660	1.355	1652	1.364	1626	1.360	1638
C6-N1	1.383		1.384		1.368		1.382	
N1-H1	1.018	3529	1.023	3460	1.023	3473	1.031	3343
C2=O2	1.224	1765	1.232	1736	1.216	1785	1.246	1666
N3-H3	1.023	3476	1.024	3468	1.057	2909	1.028	3424
C4=O4	1.226	1731	1.230	1713	1.288	1651	1.241	1697
C5-F	1.353	1232	1.352	1238	1.347	1260	1.345	1252
C6-H6	1.088	3174	1.088	3168	1.092	3136	1.090	3157
N1-H1 bending		1454		1461		1438		1466
N-H bending & ring deformation		1383		1393		1519		1409
N3-H3 bending		1354		1352		1427		1367
C6-H6 bending		1309		1311		1307		1316

Table S8: DFT-calculated frequencies of modes in 1200 to 1800 cm⁻¹ range, compared to experimental results for 5-FU in Ar matrix and to previous DFT-B3LYP calculations, both from the work of Ivanov et al.,⁵ and to experimental results obtained for solid 5-FU by Datt et al.⁶

	DFT This work	Experiment 5-FU in Ar	DFT B3LYP	Experiment Solid 5-FU
	<i>v</i> [cm ⁻¹]	<i>v</i> [cm ⁻¹]	<i>v</i> [cm ⁻¹]	<i>v</i> [cm ⁻¹]
C2=O2	1765	1761	1768	1771
C4=O4	1731	1742	1742	1723
C5=C6	1660	1685	1677	1665
N1-H1 bending	1454	1472	1471	
N-H bending & ring deform	1383	1401	1406	
N3-H3 bending	1354	1367	1391	
C6-H6 bending	1309	1334	1337	
C5-F	1232	1247	1253	1247

S2.7 – Initial structures used in AIMD simulations of (5-FU+16H₂O)@FAU

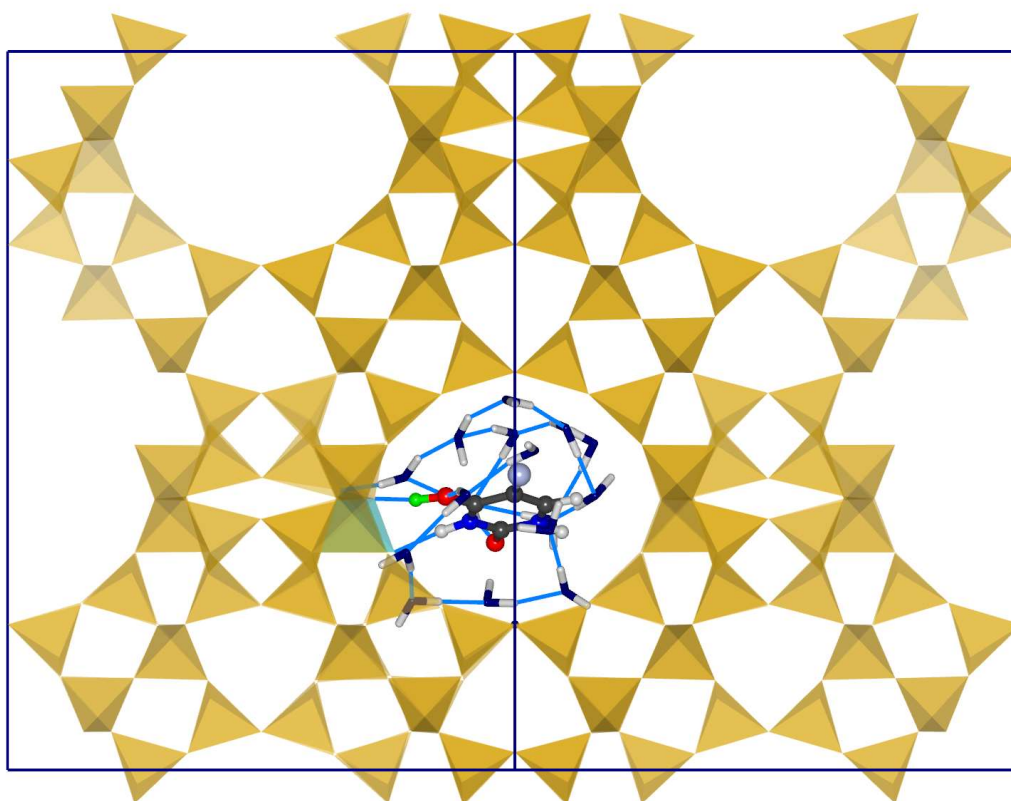


Figure S7: Starting structure of (5-FU+16H₂O)@H-FAU_1H used in AIMD simulations.

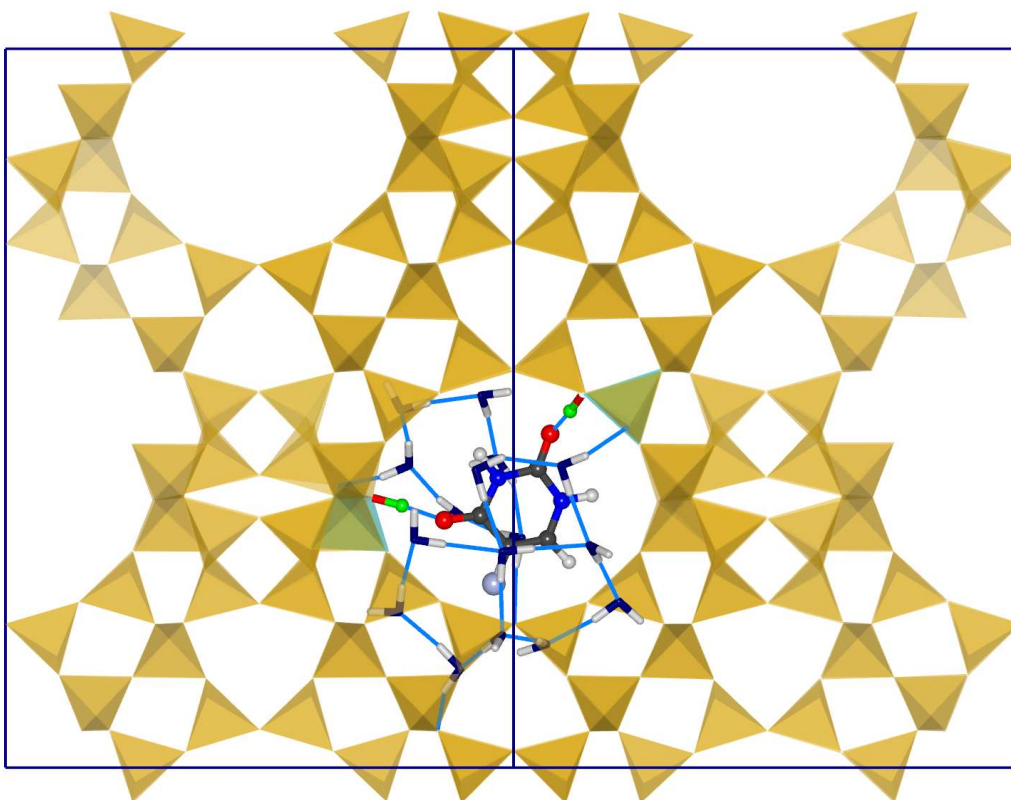


Figure S8: Starting structure of (5-FU+16H₂O)@H-FAU_2H_1_3 used in AIMD simulations.

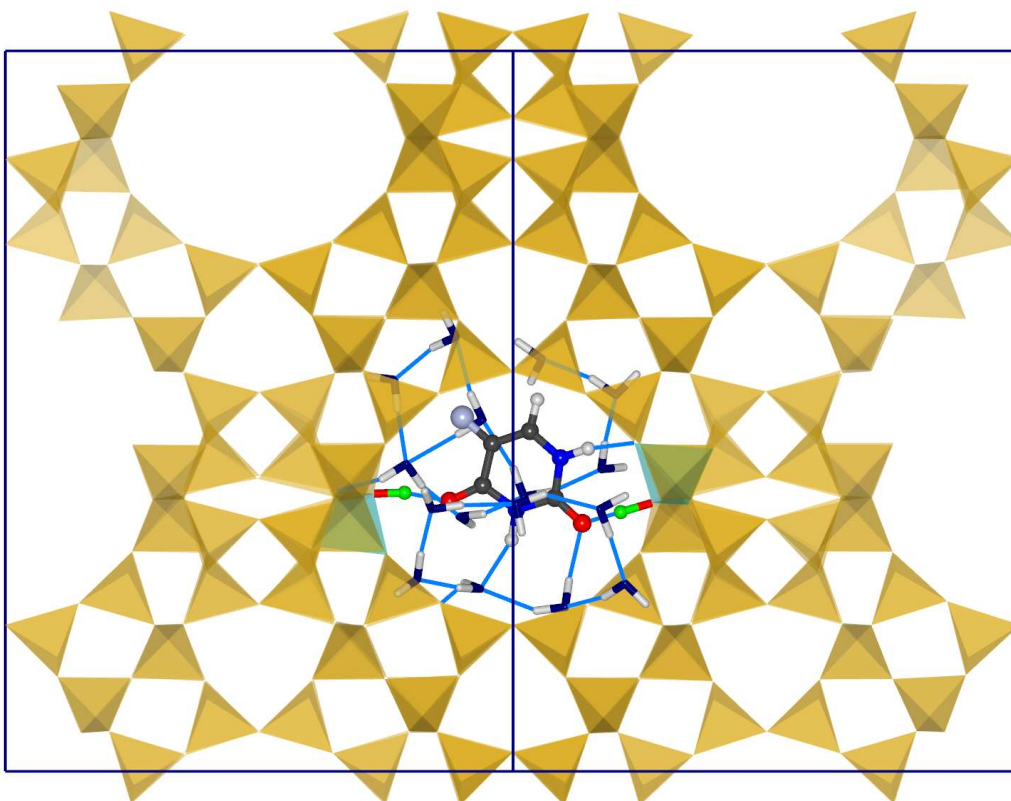


Figure S9: Starting structure of (5-FU+16H₂O)@H-FAU_2H_1_4 used in AIMD simulations.

S2.8 – RDFs obtained from AIMD simulations of (5-FU+16H₂O)@FAU

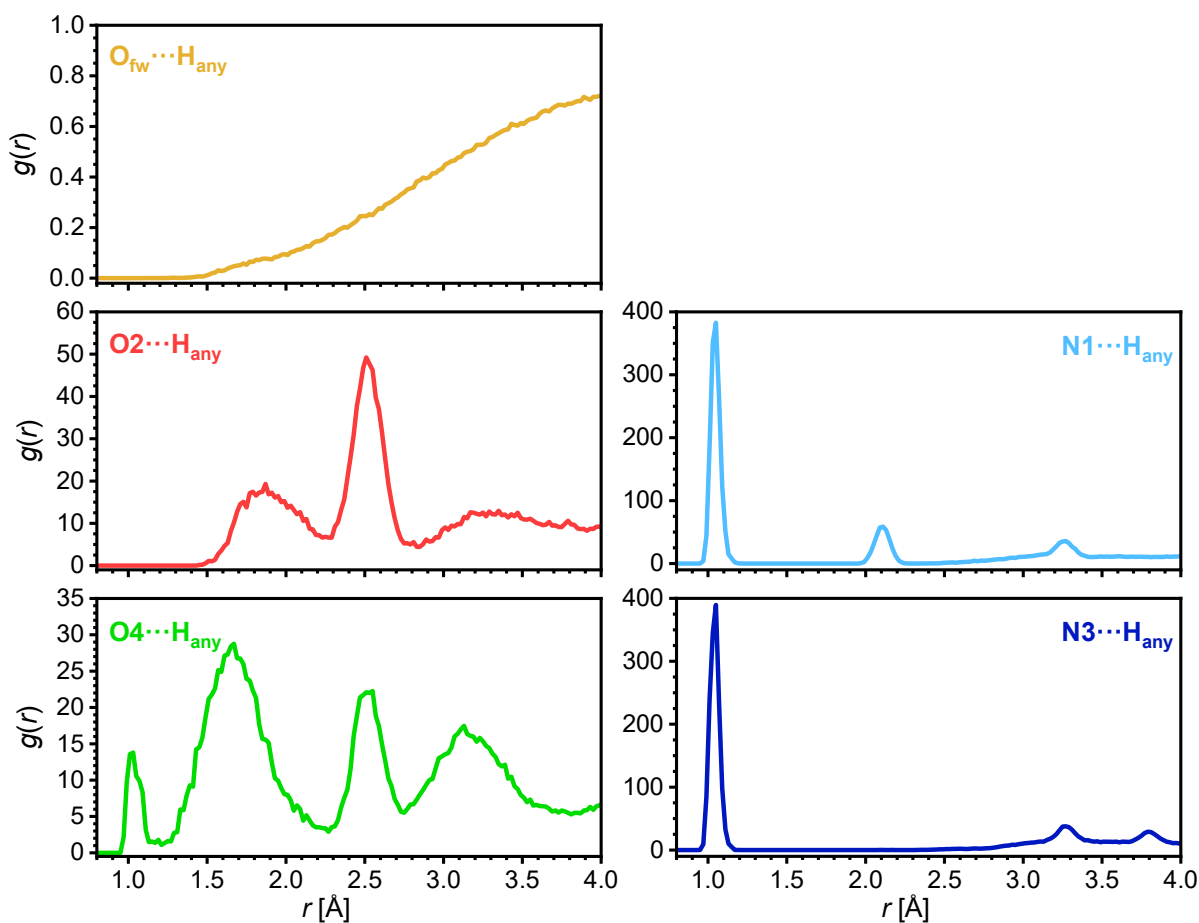


Figure S10: RDFs for selected combinations of atoms obtained from AIMD simulations of (5-FU+16H₂O)@H-FAU_1H. H_{any} encompasses all hydrogen atoms in the system.

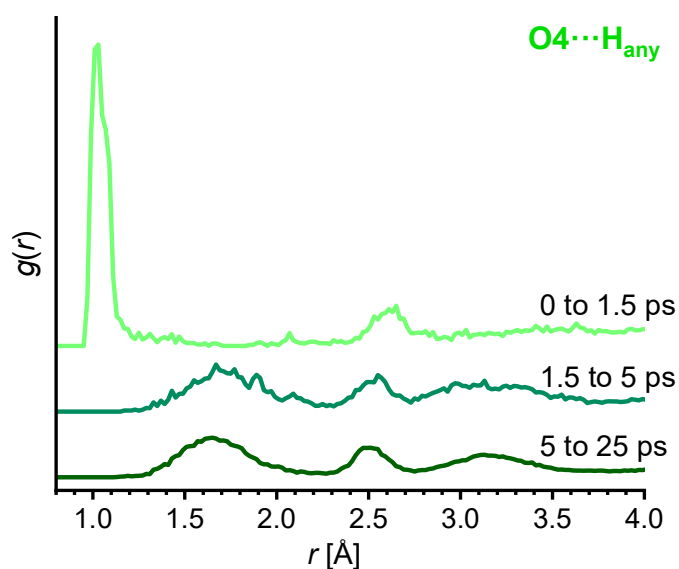


Figure S11: O4···H_{any} RDFs obtained from AIMD simulations of (5-FU+16H₂O)@H-FAU_1H computed for distinct time intervals.

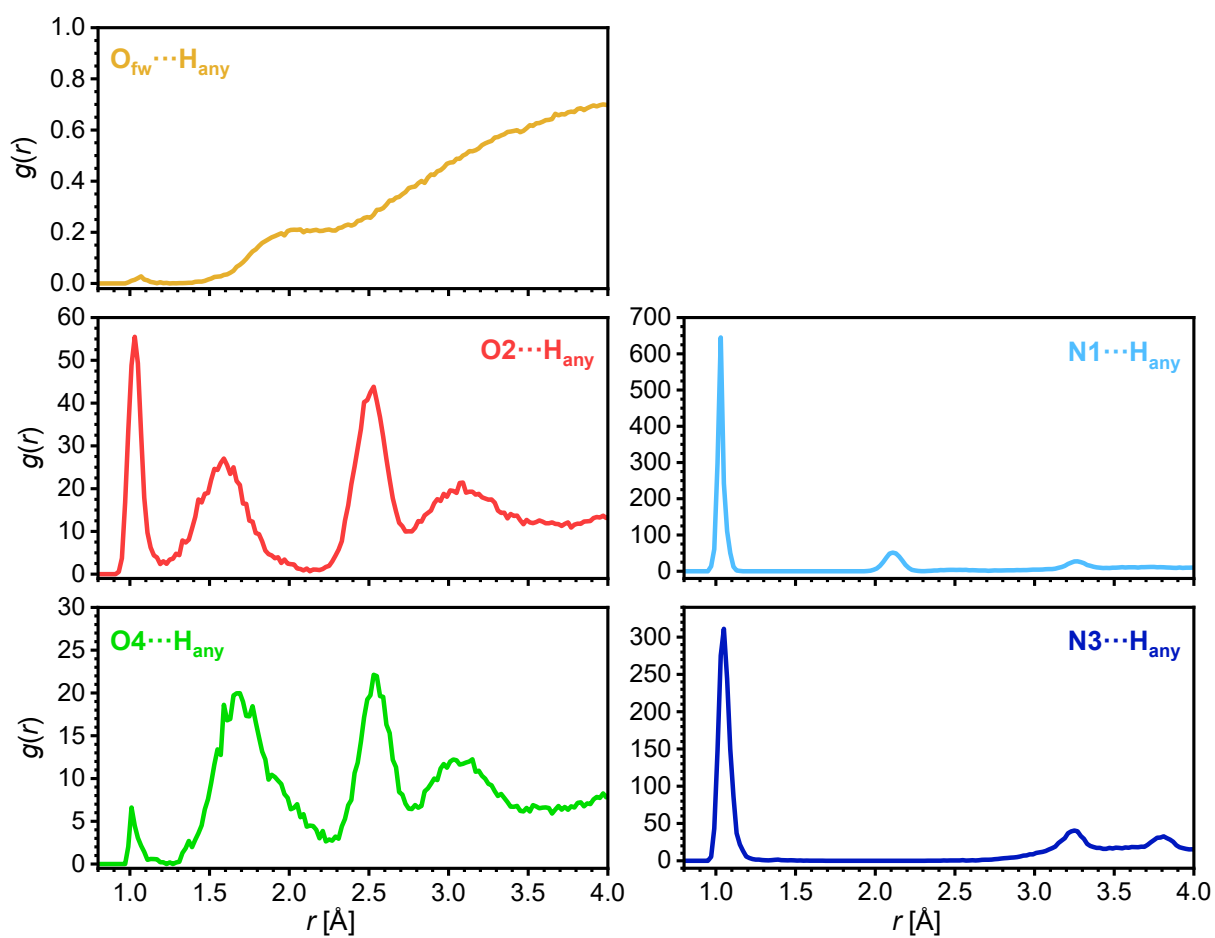


Figure S12: RDFs for selected combinations of atoms obtained from AIMD simulations of (5-FU+16H₂O)@H-FAU_2H_1_3.

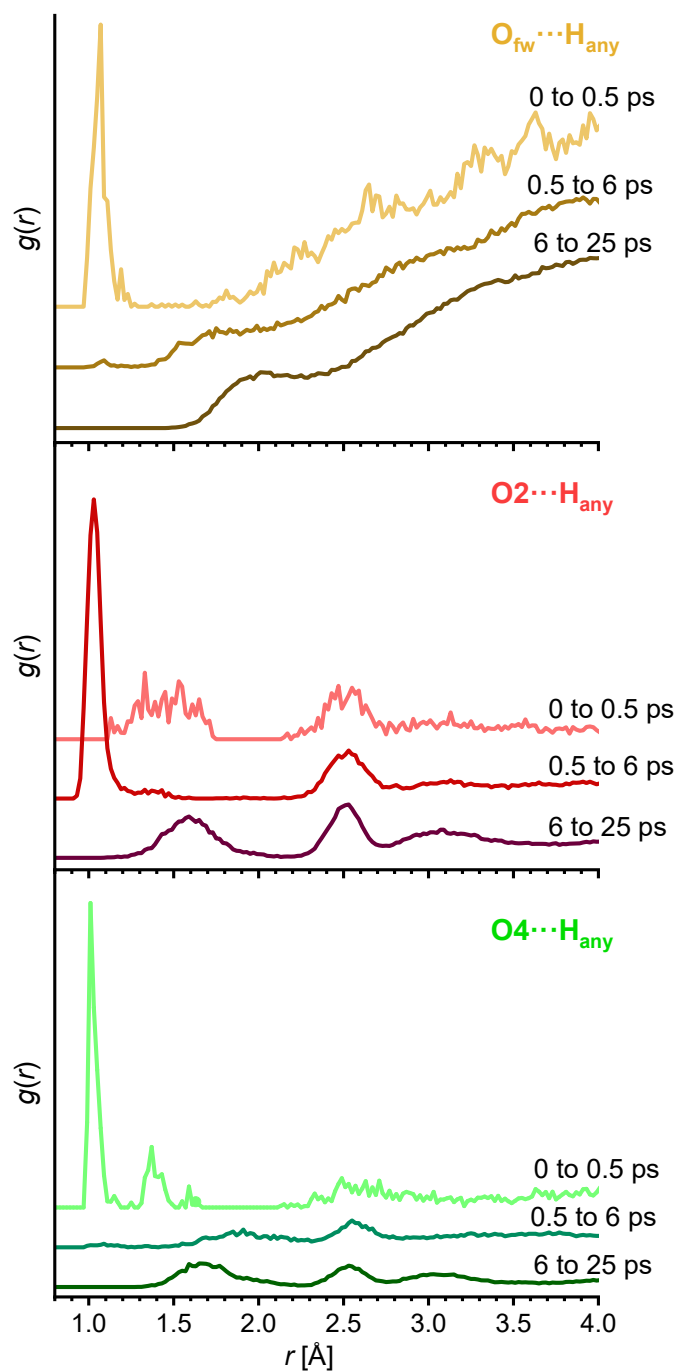


Figure S13: RDFs obtained from AIMD simulations of (5-FU+16H₂O)@H-FAU_2H_1_3 computed for distinct time intervals.

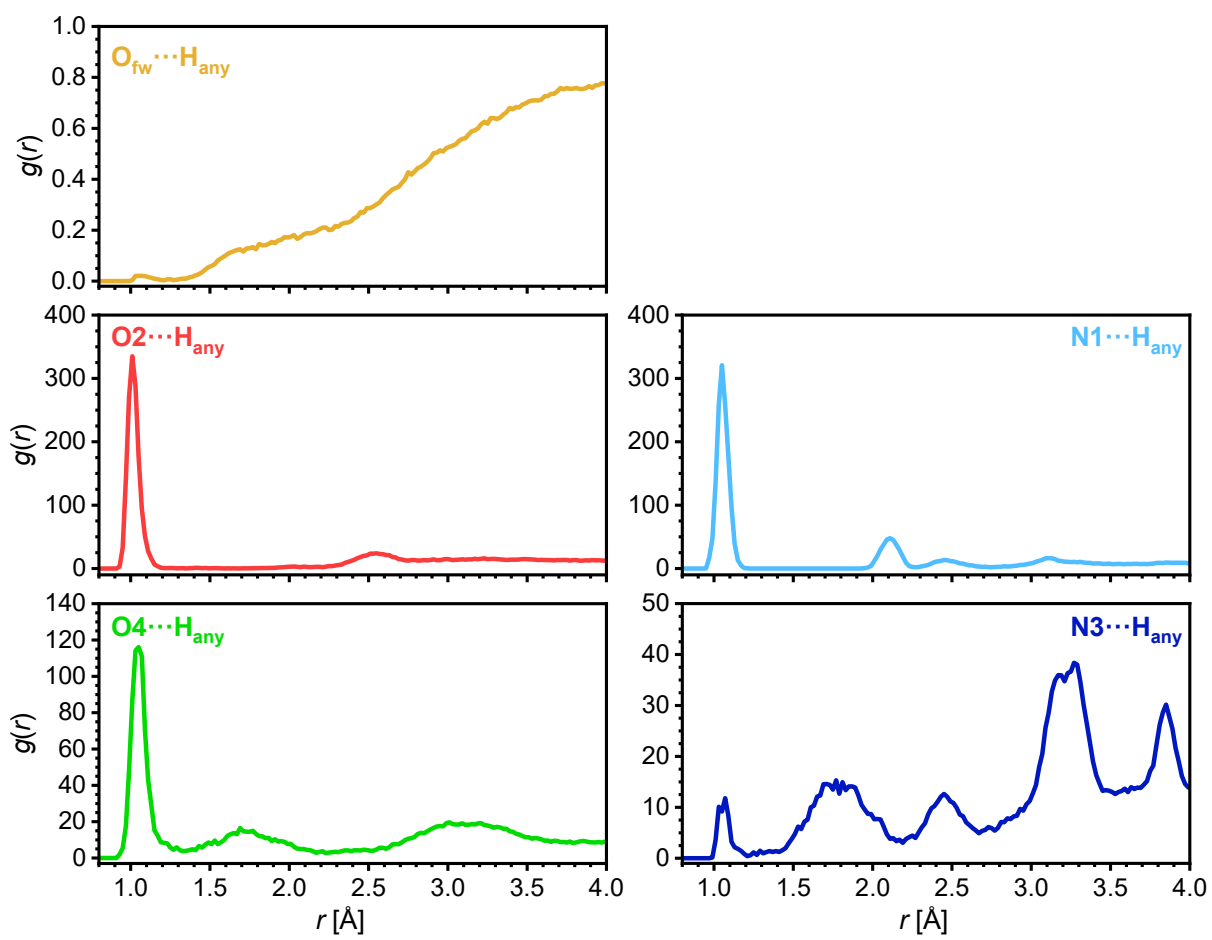


Figure S14: RDFs for selected combinations of atoms obtained from AIMD simulations of (5-FU+16H₂O)@H-FAU_2H_1_4.

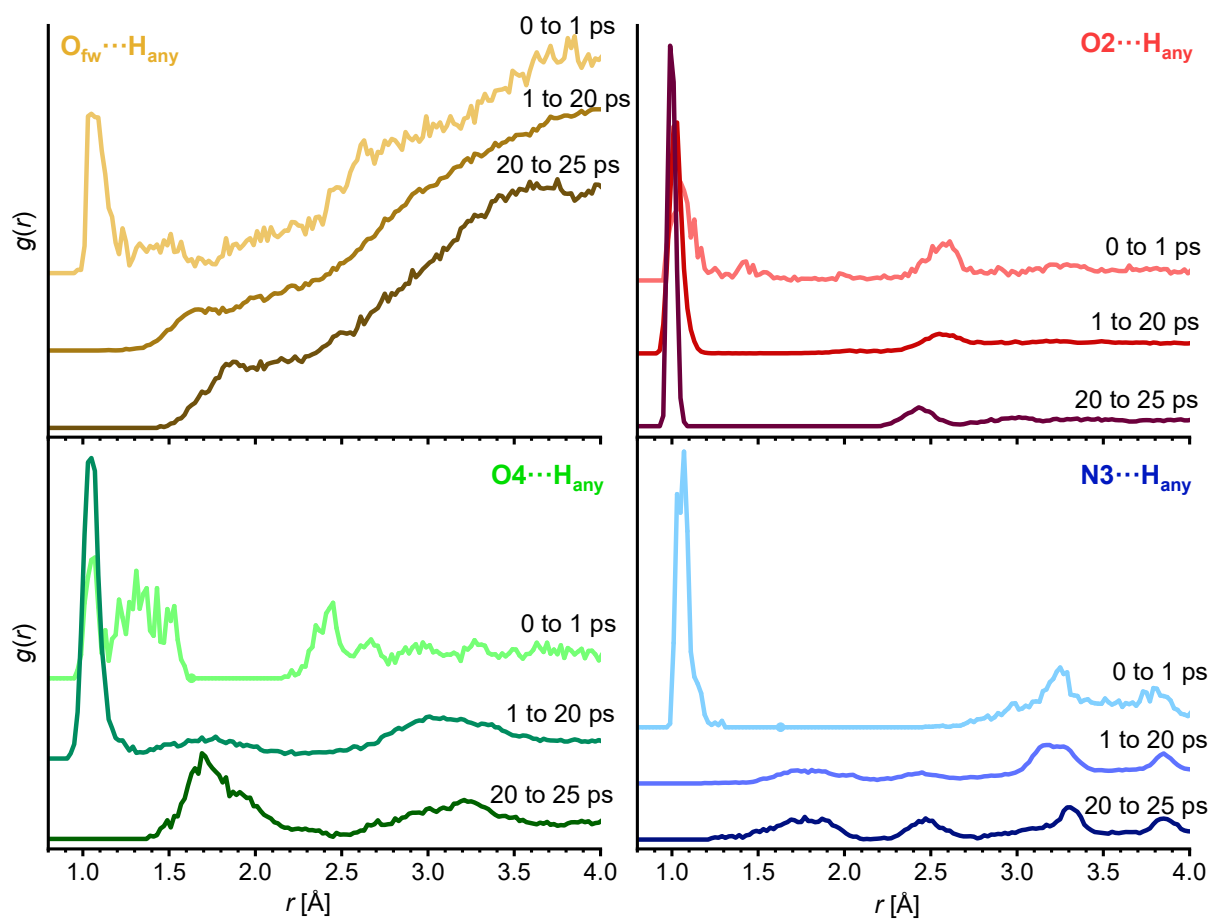


Figure S15: RDFs obtained from AIMD simulations of (5-FU+16H₂O)@H-FAU_2H_1_4 computed for distinct time intervals.

S2.9 – RDFs obtained from AIMD simulations of 5-FU in water

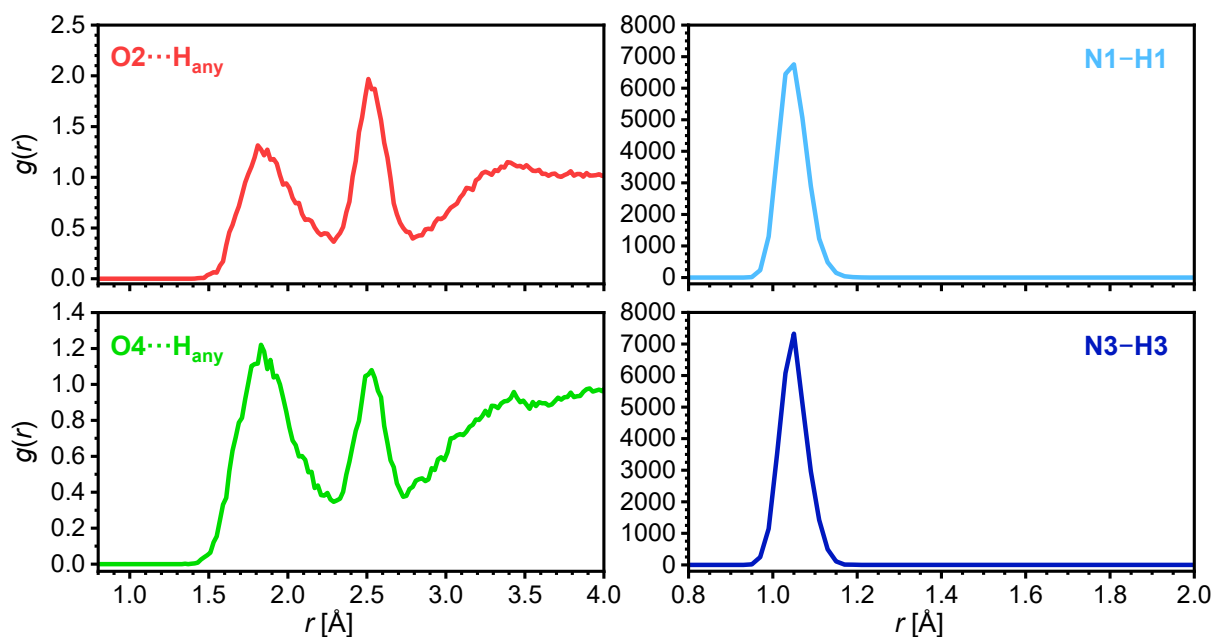


Figure S16: RDFs for selected combinations of atoms obtained from AIMD simulations of 5-FU in a box of 256 H₂O molecules.

References

- 1 H. Sun, S. J. Mumby, J. R. Maple and A. T. Hagler, *J. Am. Chem. Soc.*, 1994, **116**, 2978–2987.
- 2 M. Waldman and A. T. Hagler, *J. Comput. Chem.*, 1993, **14**, 1077–1084.
- 3 F. S. Emami, V. Puddu, R. J. Berry, V. Varshney, S. V. Patwardhan, C. C. Perry and H. Heinz, *Chem. Mater.*, 2014, **26**, 2647–2658.
- 4 C. Campaná, B. Mussard and T. K. Woo, *J. Chem. Theory Comput.*, 2009, **5**, 2866–2878.
- 5 A. Y. Ivanov, V. S. Leontiev, L. F. Belous, Y. V. Rubin and V. A. Karachevtsev, *Low Temp. Phys.*, 2017, **43**, 400–408.
- 6 A. Datt, E. A. Burns, N. A. Dhuna and S. C. Larsen, *Microporous Mesoporous Mater.*, 2013, **167**, 182–187.