Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information

Diverging effects of isotopic fractionation upon molecular diffusion of noble gases in water: mechanistic insights through *ab initio* molecular dynamics simulations

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Contents

1 Additional plots

1.1 Oxygen-oxygen radial distribution functions

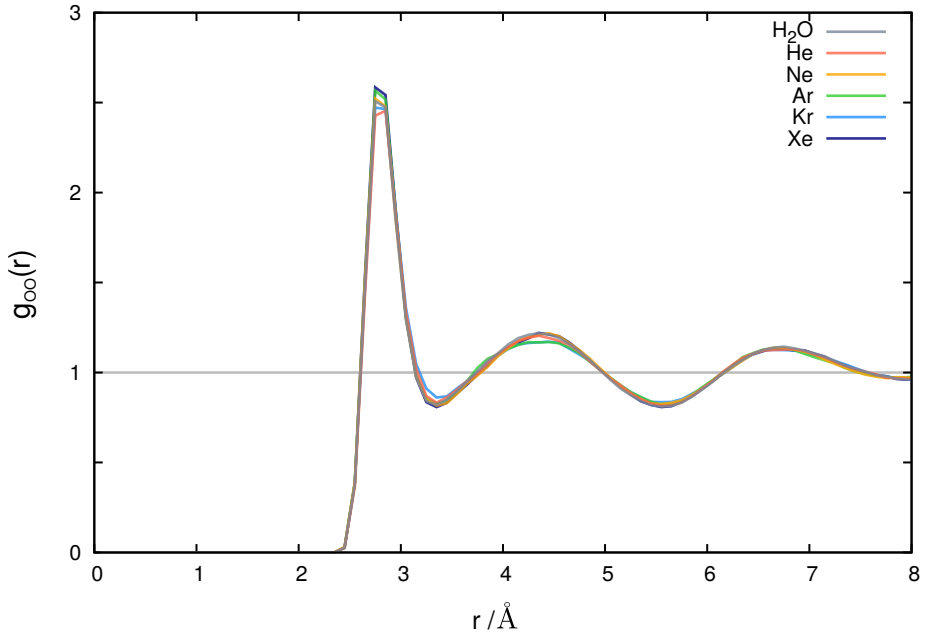

Figure 1: Radial distribution functions of oxygen-oxygen distances for the pure water reference as well as all noble gas containing systems.

1.2 Water mean-squared displacement

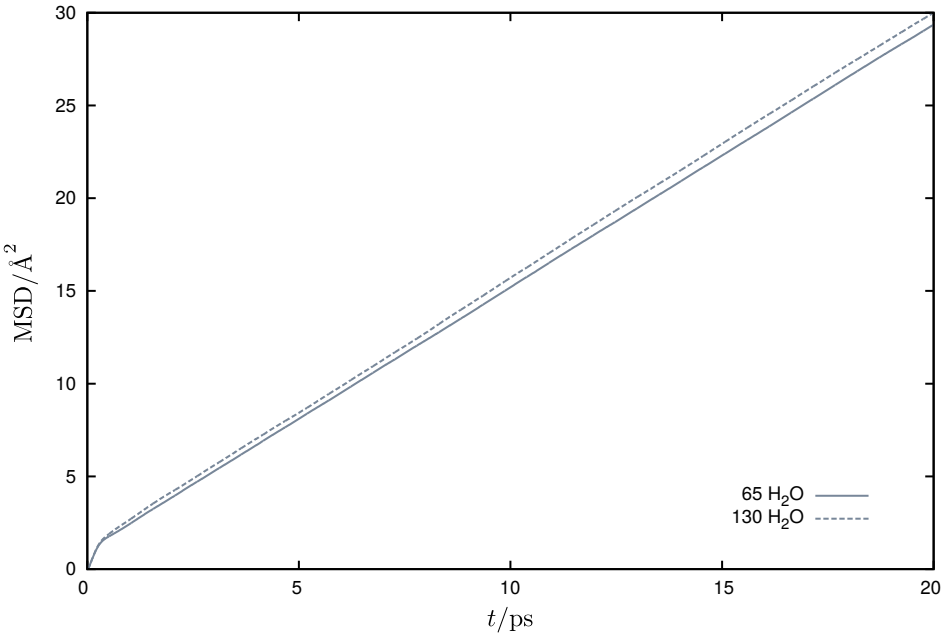

Figure 2: Mean-square displacement (of oxygen atoms) of the pure liquid water with 65 and 130 molecules.

2 Details of Symmetry Adapted Perturbation Theory analysis

2.1 Ne-H_2O dimers

	Snapshot	1	2	3	4	5
Fragment 1	Total SAPT	0.3642	0.0157	0.2587	1.4557	-0.1463
	Electrostatics	-0.4213	-0.1477	-0.3497	-1.1028	-0.0548
	Exchange	1.2731	0.4614	1.1514	3.4480	0.2159
	Induction	0.0334	-0.0087	0.0150	0.0983	-0.0377
	Dispersion	-0.5210	-0.2893	-0.5580	-0.9877	-0.2548
	Charge Transfer	0.0076	0.0023	-0.0124	-0.0424	-0.0056
Fragment 2	Total SAPT	0.2143	-0.0687	0.6853	0.0591	-0.1337
	Electrostatics	-0.3397	-0.1082	-0.6332	-0.2286	-0.0775
	Exchange	1.1019	0.3801	2.0433	0.7821	0.2962
	Induction	-0.0132	-0.0249	0.0342	-0.0154	-0.0518
	Dispersion	-0.5347	-0.3157	-0.7590	-0.4790	-0.3005
	Charge Transfer	-0.0141	-0.0055	-0.0324	-0.0114	-0.0104
Fragment 3	Total SAPT	0.2000	0.5339	-0.0005		
	Electrostatics	-0.3103	-0.5337	-0.1348		
	Exchange	1.0393	1.7851	0.4225		
	Induction	-0.0187	-0.0081	-0.0100		
	Dispersion	-0.5103	-0.7093	-0.2782		
	Charge Transfer	-0.0091	-0.0327	-0.0004		
Fragment 4	Total SAPT		-0.0724			
	Electrostatics		-0.0823			
	Exchange		0.2840			
	Induction		-0.0283			
	Dispersion		-0.2458			
	Charge Transfer		-0.0077			
Average	Total SAPT	0.2595	0.1021	0.3145	0.7574	-0.1400
	Electrostatics	-0.3571	-0.2180	-0.3726	-0.6657	-0.0662
	Exchange	1.1381	0.7276	1.2058	2.1151	0.2560
	Induction	0.0005	-0.0175	0.0131	0.0414	-0.0448
	Dispersion	-0.5220	-0.3900	-0.5318	-0.7334	-0.2777
	Charge Transfer	-0.0052	-0.0109	-0.0151	-0.0269	-0.0080

Table 1: Pair-wise intermolecular interactions and their components of the Ne with an individual next-neighboring water molecule from the first solvent shell. The values were obtained by SAPT2+3(CCD) analysis and are given in kcal/mol. The cut-off of the solvent shell around the noble gas was chosen to be the maximum of the first peak in the corresponding radial distribution function, hence only considering the closest water molecules. The snapshots are at least 5 ps appart.

2.2 Ar-H_2O dimers

	Snapshot	1	2	3	4	5
Fragment 1	Total SAPT	0.4805	-0.1243	0.5676	-0.2262	-0.0822
	Electrostatics	-0.9105	-0.3019	-1.0082	-0.2614	-0.3426
	Exchange	3.4775	0.8798	2.9082	0.9889	1.0054
	Induction	-0.6498	-0.0610	-0.1230	-0.1527	-0.0546
	Dispersion	-1.4368	-0.6412	-1.2094	-0.8010	-0.6904
	Charge Transfer	-0.3383	-0.0418	-0.1295	-0.0703	-0.0438
Fragment 2	Total SAPT	-0.2102	-0.1635	-0.1708	-0.2717	
	Electrostatics	-0.2991	-0.3328	-0.3938	-0.1969	
	Exchange	0.9124	1.0081	1.2282	0.6081	
	Induction	-0.1158	-0.1111	-0.1347	-0.0862	
	Dispersion	-0.7077	-0.7277	-0.8705	-0.5967	
	Charge Transfer	-0.0453	-0.0495	-0.0560	-0.0325	
Fragment 3	Total SAPT			0.1115		
	Electrostatics			-0.6167		
	Exchange			1.9000		
	Induction			-0.1543		
	Dispersion			-1.0174		
	Charge Transfer			-0.0881		
Fragment 4	Total SAPT			-0.1900		
	Electrostatics			-0.3060		
	Exchange			0.9218		
	Induction			-0.1077		
	Dispersion			-0.6981		
	Charge Transfer			-0.0462		
Average	Total SAPT	0.1351	-0.1439	0.0796	-0.2489	-0.0822
	Electrostatics	-0.6048	-0.3174	-0.5812	-0.2291	-0.3426
	Exchange	2.1950	0.9439	1.7395	0.7985	1.0054
	Induction	-0.3828	-0.0861	-0.1299	-0.1195	-0.0546
	Dispersion	-1.0723	-0.6844	-0.9489	-0.6988	-0.6904
	Charge Transfer	-0.1918	-0.0457	-0.0800	-0.0514	-0.0438

Table 2: Pair-wise intermolecular interactions and their components of the Ar with an individual next-neighboring water molecule from the first solvent shell. The values were obtained by SAPT2+3(CCD) analysis and are given in kcal/mol. The cut-off of the solvent shell around the noble gas was chosen to be the maximum of the first peak in the corresponding radial distribution function, hence only considering the closest water molecules. The snapshots are at least 5 ps appart.

2.3 Kr-H_2O dimers

	Snapshot	1	2	3	4	5
Fragment 1	Total SAPT	-0.1608	0.5086	-0.2971	-0.2191	0.5748
	Electrostatics	-0.3661	-1.2416	0.7010	-0.3275	-1.1422
	Exchange	1.0478	3.7036	-0.2047	1.0059	3.3972
	Induction	-0.1267	-0.4591	-0.1252	-0.1431	-0.2781
	Dispersion	-0.7157	-1.4944	-0.6681	-0.7543	-1.4020
	Charge Transfer	-0.0541	-0.2107	-0.0402	-0.0529	-0.1931
Fragment 2	Total SAPT	-0.3166	-0.3077	-0.1880	-0.2079	0.0075
	Electrostatics	-0.1684	-0.2808	-0.4711	-0.2858	-0.7601
	Exchange	0.5337	0.9050	1.3745	0.8175	2.2839
	Induction	-0.0961	-0.1639	-0.2309	-0.1128	-0.3377
	Dispersion	-0.5858	-0.7680	-0.8606	-0.6268	-1.1786
	Charge Transfer	-0.0254	-0.0471	-0.0739	-0.0438	-0.1100
Fragment 3	Total SAPT	-0.1402	-0.1899	-0.0151	-0.2522	
	Electrostatics	-0.3481	-0.3254	-0.5032	-0.2504	
	Exchange	0.9977	1.0563	1.4815	0.7306	
	Induction	-0.0923	-0.1574	-0.1114	-0.1481	
	Dispersion	-0.6975	-0.7634	-0.8820	-0.5843	
	Charge Transfer	-0.0426	-0.0634	-0.0615	-0.0465	
Fragment 4	Total SAPT	-0.3029		-0.1000	0.1329	
	Electrostatics	-0.1972		-0.4247	-0.7151	
	Exchange	0.5798		1.2641	2.0977	
	Induction	-0.1341		-0.1123	-0.1793	
	Dispersion	-0.5515		-0.8271	-1.0704	
	Charge Transfer	-0.0376		-0.0566	-0.1057	
Fragment 5	Total SAPT	-0.1512			0.0778	
	Electrostatics	-0.5759			-0.6195	
	Exchange	1.0210			1.9614	
	Induction	-0.1131			-0.2021	
	Dispersion	-0.6977			-1.0620	
	Charge Transfer	-0.0500			-0.1054	
Fragment 6	Total SAPT	-0.1608				
	Electrostatics	-0.3661				
	Exchange	1.0478				
	Induction	-0.1267				
	Dispersion	-0.7157				
	Charge Transfer	-0.0541				
Average	Total SAPT	-0.2162	0.0036	-0.1500	-0.0937	0.2912
	Electrostatics	-0.2892	-0.6159	-0.1745	-0.3947	-0.9512
	Exchange	0.8414	1.8883	0.9788	1.1629	2.8405
	Induction	-0.1152	-0.2601	-0.1449	-0.1458	-0.3079
	Dispersion	-0.6532	-1.0086	-0.8094	-0.7589	-1.2903
	Charge Transfer	-0.0428	-0.1071	-0.0581	-0.0622	-0.1516

Table 3: Pair-wise intermolecular interactions and their components of the Kr with an individual next-neighboring water molecule from the first solvent shell. The values were obtained by SAPT2+3(CCD) analysis and are given in kcal/mol. The cut-off of the solvent shell around the noble gas was chosen to be the maximum of the first peak in the corresponding radial distribution function, hence only considering the closest water molecules. The snapshots are at least 5 ps appart.