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**A molecular dynamics study of the interaction of water with external surface
of silicalite-1**

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ELECTRONIC SUPPLEMENTARY INFORMATION

1 Water characteristics with modified SPCFw water model

1.1 Bulk water properties.

Characteristics of water with the modified SPCFw model (mSPCFw) were calculated for a system of 343 H₂O molecules at the temperature 298 K and the equilibrium density. The latter was obtained by averaging the instantaneous system density over the last 4 ns of a 5 ns NPT MD simulation; the pressure and the temperature were controlled via a Berendsen barostat and via a chain of Nosé-Hoover thermostats, respectively. The bulk water properties were computed from results of MD simulation within the NVT statistical ensemble. The simulation was run for 6 ns from which the first 1000 ps were used for the equilibration and the trajectory was saved each 0.1 ps for the last 5 ns for subsequent analysis.

Table S1: Bulk water properties of mSPCFw model compared to those of the original SPCFw and SPC models, and to experimental data.

Properties ^a	mSPCFw	SPCFw ¹	SPC ¹	Expt. ^b
$\langle r_{\text{OH}} \rangle$, Å	1.028	1.031	1.000	0.97
$\langle \theta_{\text{HOH}} \rangle$, deg	108.9	107.69	109.47	106
$\langle \mu \rangle$, D	2.35	2.39	2.275	2.9
ρ , g/cm ³	0.991	1.012	0.977	0.997
n_1 ($r = 3.3$ Å)	4.28	4.35	2.28	4.26
n_2 ($r = 5.5$ Å)	22.52	22.86	22.01	22.39
ΔH_{vap} , kJ mol ⁻¹	43.24	44.85	44.18	44.02
D_s , 10 ⁻⁵ cm ² s ⁻¹	4.77	2.32	4.02	2.3
ϵ_0	70.79	79.63	66.29	78.5
G_k	3.72	3.98	3.79	
g_k	2.50	2.67	2.55	2.90
τ_D , ps	12.38	9.50	5.71	8.3
τ_2^{HH} , ps	2.36	2.01	1.15	2.0
τ_2^{μ} , ps	1.79	1.72	1.05	1.9

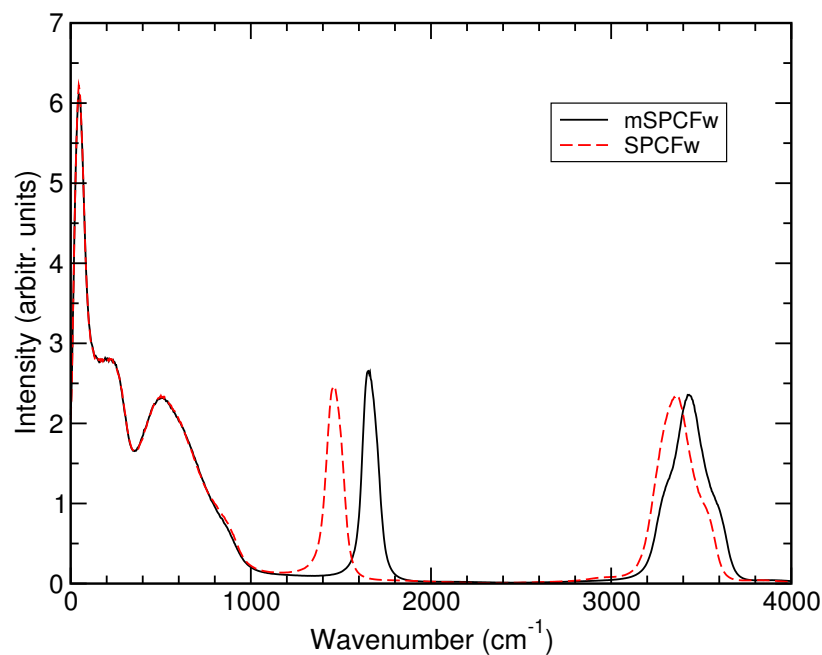
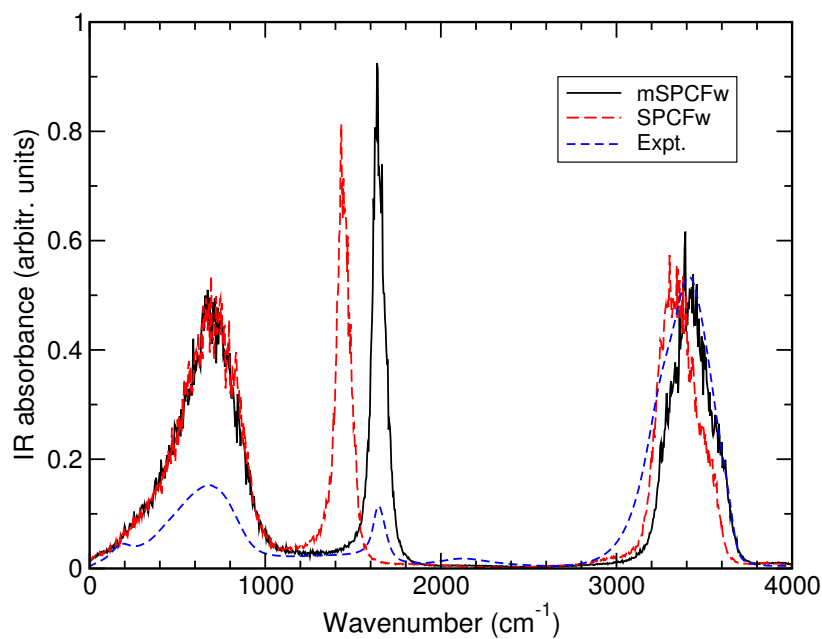
^a See definition of properties in ref¹. ^b See references in the footnotes of Table II in ref¹.

1.2 Density of vibrational states and infrared spectrum of water

Vibrational spectra were computed for both the bulk water and an isolated molecule. The former system is that described above, the latter was mimicked by an H₂O molecule in a matrix of 255 argon atoms at 100 K (above the melting temperature of argon). The MD simulations were run within the NVT statistical ensemble for the period of 40 ps and the trajectory was saved each 4 fs for the last 20 ps. The spectra of bulk water were averaged over 25 runs starting from different initial conditions, the power spectrum of H atoms of isolated molecule was obtained as the average over 100 runs. Table S2 compares the frequencies of vibrational modes for the isolated H₂O molecule computed with the mSPCFw and SPCFw models with experimental data.² Figures S1 and S2 display the density of vibrational states and the infrared spectrum of bulk water, respectively.

Table S2: Frequencies (in cm^{-1}) of vibrational modes of isolated H_2O molecule.

Mode	Description	mSPCFw	SPCFw	Expt. ²
ν_1	Sym. OH stretching	3665	3606	3657
ν_2	HOH angle-bending	1593	1380	1595
ν_3	Asym. OH stretching	3753	3688	3756

**Figure S1:** Density of vibrational states of bulk liquid water computed with the SPCFw and mSPCFw models.**Figure S2:** Infrared spectra of bulk liquid water computed with the SPCFw and mSPCFw models in comparison with the experimental spectrum.³

2 Computational procedure.

2.1 Simulated annealing calculations

Simulated annealing (SA) calculations started from 20 snapshot configurations evenly chosen along the MD trajectory at 150 K. In each SA calculation the temperature of the system was gradually reduced to 1 K during 150 ps (300000 time-steps) by rescaling the target temperature each 2000 time-step. The simulation between the rescalings was performed in the NVT ensemble using the chain of Nosé-Hoover thermostats. The visual inspection of final configurations allowed revealing the adsorption site shown in Figure 2c.

References

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