**Supplementary material:**

# Protonation of water clusters in the cavities of acidic zeolites: $(H_2O)_n$·H-CHA, *n*=1-4

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**Table S1.** Selected harmonic frequencies ($cm^{-1}$) calculated for the 1:1 complex[a)]

| PBE | BLYP | Assignment[a)] | Experiment[b)] |
|---|---|---|---|
| 3720 | 3685 | $\nu(O_hH)$ | 3670 |
| 3589 | 3571 | $\nu(O_hH_b)$ | 3540 |
| 2408 (1289)[d)] | 2544 (1110)[d)] | $\nu(O1H_{bh})$ | ~ 2710[c)] (2875; 2400) (~910)[d)] |
| 1569 | 1574 | $\delta(H_2O_h)$ | 1630 |
| 1413 | 1402 | $\delta(O1H_{bh})$ | 1406, 1380; 1355[e)] |
| 976 | 938 | $\gamma(O1H_{bh})$ | 795, 765[f)] |

[a)] $\nu$, $\delta$, and $\gamma$ denote stretching, in-plane and out-of-plane bending modes, respectively. For atomic labels see Fig. 2. [b)] Frequencies obtained for a coverage of ~ 1 water per acid site [20]. [c)] Minimum of AB doublet (maxima in parenthesis) due to FERMI resonance with overtone of $\delta(O1H_{bh})$ [20]. [d)] Shift with respect to dry zeolite. [e)] Estimated from the minimum of the AB doublet at 2710 $cm^{-1}$ [20].[f)] For $H_2O$ adsorbed on HSAPO-34 [17], the IR spectrum of $H_2O$ adsorbed on HSSZ-13 was measured in the 3750 – 1360 $cm^{-1}$ range only [20].

**Table S2**. Relative stabilities, ΔE (kJ/mol), and selected interatomic distances (Å) of different NC and IP species, corresponding to minima on the BLYP potential energy surface of the 2:1 complex.[a]

| Species[b] | ΔE | O1...$O_h$ | $H_{bh}$...$O_h$ | $O_h$…$O_w$ | $O_h$…$H_{bw}$ | $O_h$…O3’ | $O_w$…O4 |
|---|---|---|---|---|---|---|---|
| NC | 0.0 | 2.49 | 1.40 | 2.75 | 1.00 | 3.30 | 3.09 |
| NC | 0.3 | 2.49 | 1.39 | 2.76 | 1.00 | 3.22 | 3.12 |
| IP | 2.0 | 2.51 | 1.11 | 2.63 | 1.02 | 3.12 | 3.16 |
| IP [c] | 6.1 | 2.54 | 1.06 | 2.48 | 1.08 | 2.84 | 3.12; 2.90 |

[a] The atomic labels are the same as in Fig. 3.

[b] NC - neutral complex, IP – ion pair.

[c] In the less-stable IP species both OH groups of the second water interact with the framework oxygen atoms by weak H-bonds.

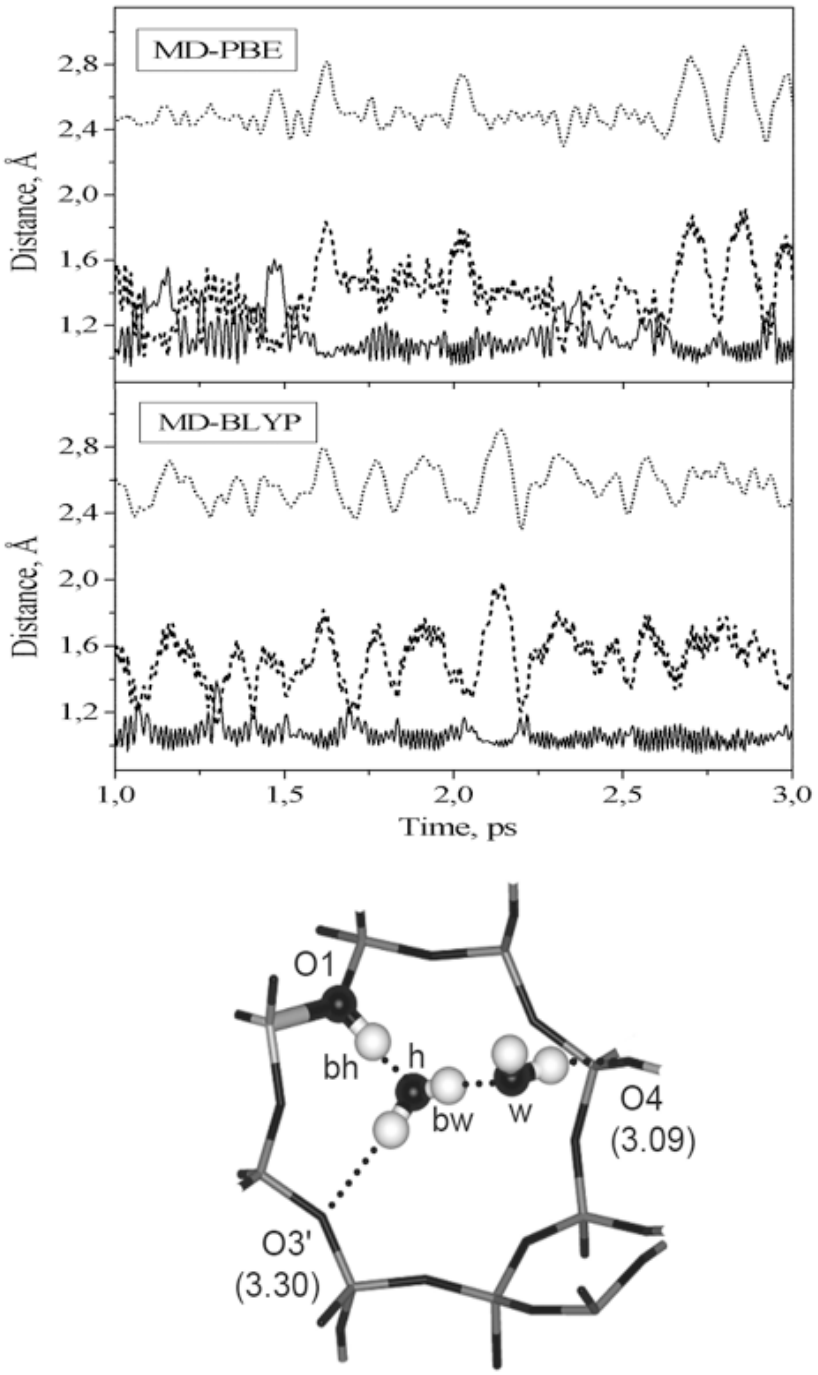


**Figure S1**. Comparison of interatomic distances obtained by molecular dynamics with BLYP and PBE for the 2:1 $H_2O$:H-CHA complex. Continuous line: O1...$H_{bh}$; broken line: $H_{bh}$ … $O_h$ ; dotted lone: O1…$O_h$, see structure in the lower part of the figure.

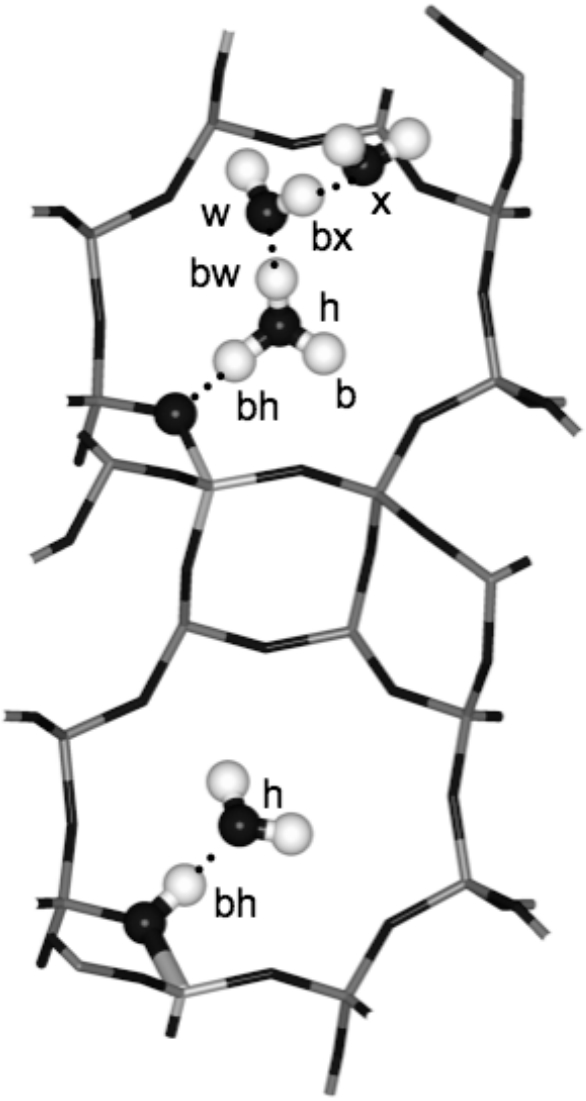


**Figure S2**. The structure of the 1:1 and 3:1 $H_2O$-H-CHA complexes in the double cell.

**Table S3.** Selected calculated harmonic frequencies ($cm^{-1}$) for the 1:1/3:1 loading (2:1 global loading)

| BLYP | PBE | Assignment[a)] |
|---|---|---|
| 3717, 3703, 3625, 3586, 3576, 3450 | 3760, 3723, 3611, 3600, 3571, 3529 | ν(OH) of OH, free or weakly H-bonded to the framework |
| 3260 | 3238 | $\nu(O_wH_{by})$ |
| 2507 | 2288 | $\nu^*(O1H_{bh})$ |
| 2380 | 2273 | $\nu(O_hH_{bw}) + \nu(O_hH_{bh})$ |
| 2060 | 1968 | $\nu(O_hH_{bh}) + \nu(O_hH_{bw})$ |
| 1674, 1654 | 1679, 1641, | $\delta(H_3O_h^+)$, $\delta(H_2O_h)$ |
| 1623, 1597, 1549 | 1616, 1588, 1551 | $\delta(H_2O_y)$, $\delta(H_2O_w)$, $\delta^*(H_2O_h)$ |
| 1418 | 1447 | $\delta^*(O1H_{bh})$ |

[a)] ν, δ, and γ denote stretching, in-plane and out-of-plane bending modes, respectively. For atomic labels see Figs. 2 and 4a. The asterisk marks the vibrations of the NC structure.