Water Adsorption on Zeolites: Ab-Initio Interpretation of IR Data

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Ab-initio 6-31G* OH frequency calculations show the water molecule complex with the bridging OH group of zeolites to be hydrogen-bonded. The experimental 3390- and 3695-cm^{-1} frequencies of the complex are interpreted to belong to the water OH group interacting with the surface by two hydrogen bonds and to the other slightly perturbed water OH group, respectively. The broad $\sim$2900-, $\sim$2450-, and $\sim$1700-cm^{-1} bands are explained on the basis of a theory of OH band profiles of hydrogen-bonded complexes to be the so-called (A, B, C) trio, caused by resonant interactions between the ν(OH) $\pm$ ν(OH···O) combination modes and the δ(OH) and γ(OH) overtones of the perturbed bridging OH group.

Introduction

Adsorption of water on Bronsted sites of zeolites has been studied with IR methods by many authors (refs 1–5 and references therein). The four OH bands at 3695, 3390, $\sim$2900, and $\sim$2450 cm^{-1} have been assigned to a water molecule complex with the bridging OH group in HZSM-5 zeolites.[2-4] This complex was suggested by Jentys et al.[3,4] to be a hydroxonium ion attached to the lattice AlOSi$^-$ acid residue. The sharp 3695-cm^{-1} band was attributed to the free OH group of the H$_3$O$^+$ ion, pointed away from the surface.[2-4] The broad bands at $\sim$2900 and $\sim$2450 cm^{-1} were proposed to be associated with the antisymmetric and symmetric H$_3$O$^+$ vibrations involving the two other OH groups bonded to the AlOSi$^-$ bridging oxygen.[3,4] The 3390-cm^{-1} band, appearing together with the three other above-mentioned bands,[3,4] was not discussed in detail.[3,4]

An ab-initio study with a DZP basis set by Sauer et al.[6] showed the water complex to be hydrogen-bonded, the one water OH group interacting both with the bridging OH group and with the nearest AlOSi oxygen, as a proton acceptor and as a proton donor, respectively, and the other OH group being free. Within the DZP approximation[6] this structure was found to be more stable, by about 18 kJ/mol, than the ion-pair structure, corresponding to the H$_3$O$^+$ ion attached by two strong hydrogen bonds to the AlO$_4^-$ lattice residue. Electron-correlation contributions estimated in this study by the MP2 method led to about the same energy of the hydrogen-bonded and ion-pair structures. Due to the known uncertainty of the MP2 approximation,[6] the authors did not come to any definite conclusion about the real nature of the adsorbed complex.

The conclusion of experimental IR studies[2-4] in favor of the H$_3$O$^+$ ion is based mainly on the assumption of the $\sim$2900- and $\sim$2450-cm^{-1} doublet belonging to the antisymmetric and symmetric vibrations of the surface H$_3$O$^+$. However, as it was shown in our recent study,[7] these two bands, detected also in the adsorption of many other basic molecules,[7] belong to the so-called (A, B, C) trio[8-11] of OH bands, at $\sim$2900, $\sim$2400, and $\sim$1700 cm^{-1}, typical for medium-strong and strong hydrogen-bonded complexes in vapors, liquids, and solids (refs 8–11 and references therein). According to a theory of OH bond profiles of hydrogen-bond complexes,[8-11] they are caused by resonant interactions between the ν(OH) stretching vibration and the δ-

TABLE I: Bond Lengths, AB (Å), and Angles, ABC and ABCD^a (deg)

molecule	geometry
1^b	OH^1, 0.947; OH^2, 0.955; H^{1}OH^2, 106.2; H^{1}OH^{2}X, 129.9; H^{2}OXO, 2.9
2^c	AlO^1, 1.917; AlO^3, 1.751; AlO^4, 1.712; AlO^5, 1.723; O^{1}H^4, 0.953; O^{3}H, 0.944; O^{4}H, 0.942; O^{5}H, 0.942; O^{1}H^1 0.975; H^{1}O^2, 1.737; O^{2}H^2, 0.948; O^{2}H^3, 0.963; O^{1}AlO^3, 96.7; O^{1}AlO^4, 107.1; O^{1}AlO^5, 93.8; AlO^{1}H^4, 108.9; AlO^{3}H, 122.2; AlO^{4}H, 108.5; AlO^{5}H, 127.2; AlO^{1}H^1, 113.5; O^{1}H^{1}O^2, 158.6; H^{1}O^{2}H^3, 89.6; H^{2}O^{2}H^3, 106.4; O^{3}AlO^{1}O^5, –118.0; O^{4}AlO^{1}O^5, 1.1; H^{1}O^{1}AlO^5, 113.6; O^{2}H^{1}O^{1}Al, –3.1; H^{3}O^{2}H^{1}O^1, –3.7;H^{2}O^{2}H^{3}H^1, –118.1
3^d	AlO^1, 1.908; AlO^3, 1.749; AlO^4, 1.718; O^{1}H^4, 0.948; O^{3}H, 0.944; O^{4}H, 0.942: O^{1}H^1, 0.968; H^{1}O^2, 1.748; O^{2}H^2, 0.946; O^{2}H^3, 0.961; O^{1}AlO^3, 95.4; O^{3}AlO^4, 117.1; AlO^{1}H^4, 126.1; AlO^{3}H, 122.0; AlO^{4}H, 125.9; AlO^{1}H^1, 120.8; O^{1}H^{1}O^2, 150.2; H^{3}O^{2}H^1, 93.5; H^{2}O^{2}H^3, 109.1; O^{4}AlO^{3}O^1, 106.1

^{a} Dihedral angle. ^{b} C_3 point group symmetry. X is the point of the C_3 axis crossing the OOO plane. ^{c} The HO^{3}AlO^1, HO^{4}AlO^1, and HO^{5}AlO^1 angles were taken to be 180°; all the other geometry parameters are optimized. ^{d} C_s point group symmetry.

TABLE II: Total Energies (hartrees)

structure	energy
1	–228.0581
2	–620.4764
3	–620.4703

(OH) and γ(OH) overtones of the strongly perturbed bridging OH group (see below). This shows the adsorbed water to be in a hydrogen-bonded form, apparently like that found in ref 6. Owing to the difficulties of discriminating between the hydrogen-bonded and ion-pair structures on the basis of energy calculations (see ref 6 for more details), a theoretical support for the hydrogen-bonded structure will be based on the OH frequency calculations.

Theoretical Method

Ab-initio SCF calculations were performed with the 6-31G* basis set using the GAUSSIAN-90 package.[12] Optimized geometries and total energies of the molecules are presented in Tables I and II, respectively.

Results and Discussion

To demonstrate the reliability of the adopted approximation, in Table III the calculated and experimental[13] OH frequency shifts of the water trimer (1, Figure 1) are presented, with each water molecule interacting by means of two hydrogen bonds
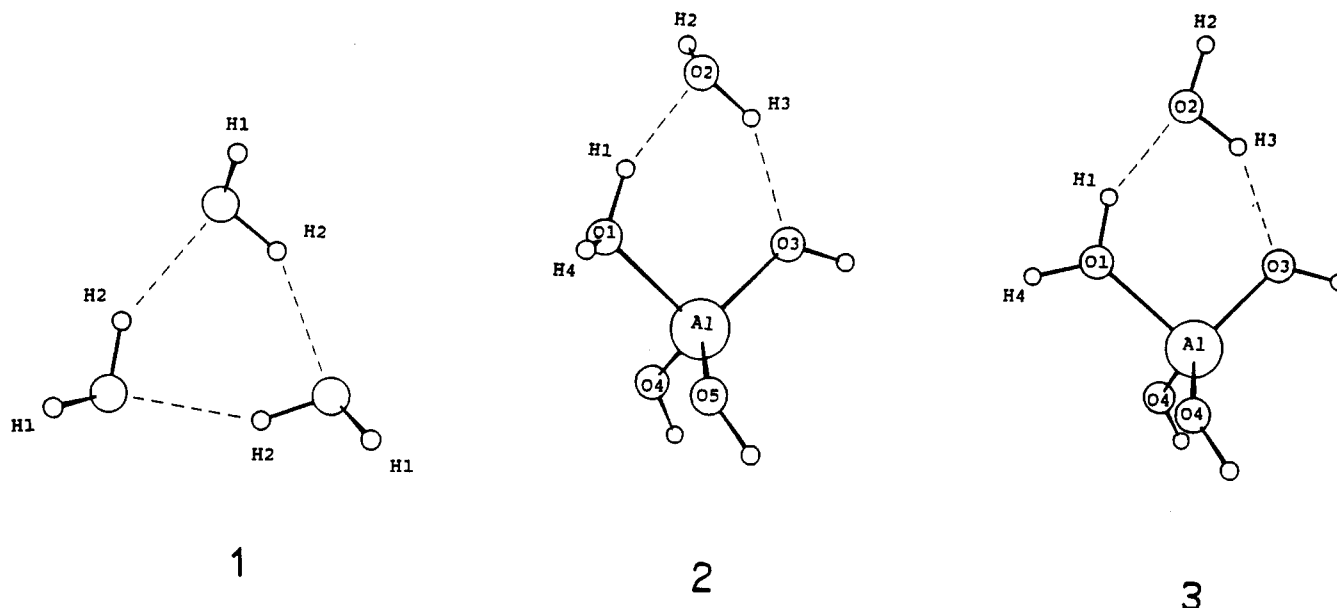
Figure 1. Molecular structures.

TABLE III: OH Frequency Shifts[a] (cm⁻¹)

structure	assignment	calcd	obsd[b]
1	$\nu(OH_{nb})$	24	20
	$\nu(OH_b)$	-136	-171
1′	$\nu(OH_{nb})$	7	

[a] With respect to the uncoupled O–H vibrator frequency of the HOD molecule. [b] Reference 13.

TABLE IV: 6-31G* OH Frequencies (cm⁻¹)

structure	assignment[a]	freq
1	$\nu(OH_{nb})$ (90) + $\nu(OH_b)$ (10)	4155
	$\nu(OH_{nb})$ (13) + $\nu(OH_b)$ (87)	3995
1′	$\nu(OH_{nb})$ (100)	4138
2	$\nu(OH_{nb})$ (97) + $\nu(OH_{wb})$ (3)	4135
	$\nu(OH_{nb})$ (7) + $\nu(OH_{wb})$ (93)	3859
3	$\nu(OH_{nb})$ (96) + $\nu(OH_b)$ (4)	4174
	$\nu(OH_{nb})$ (10) + $\nu(OH_b)$ (90)	3883

[a] Numbers in parentheses indicate the contribution of localized vibrations to each normal mode, estimated from the normalized sums of the squares of the eigenvectors of each atom for each mode.

like in the hydrogen-bonded structure suggested by Sauer et al.[6] As the coupling between the nonbonded and bonded O–H vibrators in the complex is quite small (see contributions of localized vibrations to the normal OH modes in Table IV), their ν_{nb} and ν_b shifts with respect to the uncoupled water O–H vibrator frequency $\nu°(OH)$ are used, being the most appropriate of the OH vibration characteristics[14] for water structure analysis in complex hydrogen-bonded aggregates. The $\nu°(OH)$ is taken to be the HOD $\nu(OH)$, the experimental and 6-31G* values being 3687[13] and 4131 cm⁻¹. An important feature of the interaction is that the $\Delta\nu_{nb} = 24$ cm⁻¹ is positive (Table III). As follows from the calculations, this positive shift is provided not only by the coupling effect, the contribution being

$$\Delta\nu_{coupl} = \nu_{nb}(1) - \nu_{nb}(1') = 17 \text{ cm}^{-1} \qquad (1)$$

where 1′ is the trimer (Figure 1) with the O–H_b vibrators replaced by the O–D_b vibrators, but also by the O–H_{nb} bond strengthening, as $\Delta\nu_{nb}(1') = 7$ cm⁻¹ (Table III). The literature data (ref 15 and references therein) show such O–H_{nb} strengthening to be a general phenomenon for hydrogen-bonded complexes.

The full optimization of the water position with respect to the $H_2O \cdot Al(OH)_4$ molecular analog of the bridging OH group led to structure 2 (Figure 1), which is in good agreement with the experimental OH frequency shifts (Table V). As distinct from

TABLE V: OH Frequency Shifts[a] (cm⁻¹)

	calcd		
assignment	2	3	obsd[b]
$\nu(OH_{nb})$		43	
$\nu(OH_{wb})$	4		8
$\nu(OH_b)$	-273	-248	-297

[a] With respect to the uncoupled O–H vibrator frequency of the HOD molecule. [b] The 3695- and 3390-cm⁻¹ frequency[3,4] shifts.

the case of structure 3 optimized with the C_s symmetry constraint, like that reported in ref 6, in 2 the O^2–H^2 bond is strongly shifted from the $O^1O^2O^3$ plane and slightly weakened (cf. the calculated $R(O^2H^2) = 0.9482$ Å of 2, $R(O^2H^2) = 0.9456$ Å of 3, and $R(OH)$ = 0.9474 Å of free molecular water). Considering the effect of O–H_{nb} strengthening in hydrogen-bonded complexes[15] (see above), this weakening has to be due to a weak H^2 bond to the nearest O^1 and O^3 oxygens in structure 2, $R(H^2O^1) = 3.23$ Å and $R(H^2O^3)$ = 3.21 Å. Therefore structure 3, with the O^2–H^2 vibrator being nonbonded, overestimates the highest OH frequency of the adsorbed water significantly (Table V). We consider structure 2 to be a molecular analog for the water adsorption on the bridging OH group of zeolites, with the O–H_b and O–H_{wb} (weakly bonded) vibrators being responsible for the strongly and slightly shifted 3390- and 3695-cm⁻¹ frequencies,[2-4] with respect to the $\nu°(OH)$.

As shown in our recent experimental and theoretical study,[7] there is a very interesting phenomenon in interactions of basic molecules with the bridging OH group of zeolites, which makes the $\Delta\nu(OH)$ of this group not correspond to any observable OH band maximum. The broad bands at ~2900, ~2450, and ~1700 cm⁻¹, reported in the literature for more than 15 different adsorption complexes on the bridging OH groups,[7] including the water complex, belong to the so-called (A, B, C) trio,[7] well-known for strong hydrogen-bonded complexes in vapors, liquids, and solids.[8-11] In terms of the theory of OH band profiles of hydrogen-bonded complexes,[8-11] these bands, actually pseudobands, are produced by the Evans transmission windows at ~2600 and ~1800 cm⁻¹, in the very broad $\nu(OH) \pm k\nu(OH\cdots B)$ superposition band of the strongly perturbed bridging OH group. These windows result from Fermi resonances of the $\delta(OH)$ in-plane overtone at ~2600 cm⁻¹ and $\gamma(OH)$ out-of-plane overtone at ~1800 cm⁻¹ with the $\nu(OH) \pm k\nu(OH\cdots B)$ modes in the vicinity of these overtones. Other examples of this trio in adsorptions on zeolites, taken from ref 16 with our assignment of the OH bands, are presented in Table VI. According to this interpretation, the broad ~1700-cm⁻¹ band, which was detected for the water

TABLE VI: OH Pseudoband Wavenumbers[a] (cm^{-1})

adsorbed molecule	assignment		
	A	B	C[b]
water	2900	2500	
dimethyl ether	2950	2500	1900–1300
diethyl ether	2950	2300	1900–1300
tetrahydrofuran		2370	1900–1300
di-n-butyl ether	2900	2300	1900–1300
acetone	2900	2370	1800–1300
n-butyraldehyde	2900	2400	1700–1300
acetonitrile	2820	2430	
benzonitrile	2800	2360	
formic acid	2900	2460	1700–1300
acetic acid	2900	2470	1800–1300

[a] From ref 16 with our assignment on the basis of a theory of OH band profiles of hydrogen-bonded complexes.[8-11] [b] Apparently complicated by $\delta(OH) + \nu(OT)$ modes (see ref 10).

adsorption in refs 3 and 4 and could be easily found in the spectra of ref 2, also belongs to the water complex with the bridging OH group, being the C band. As shown in a recent study by Ratajczak et al.,[10] for solids the C band range can be complicated by $\delta(OH) + \nu(TO)$ combination modes, $\nu(TO)$ being a lattice vibration of the bridging OH group oxygen atom.

As the methanol complex with the bridging OH group is similar to the water complex,[17-20] the hydrogen atom of the slightly perturbed water OH group being replaced by the CH_3 group, four OH bands could be expected a priori for this complex, analogous with the 3390, ~2900, ~2450, and ~1700 cm^{-1} bands of the water complex. The four bands at ~3390, ~2900, ~2440, and ~1687 cm^{-1}, similar in shape to the above-mentioned ones for the water complex, were found in a recent IR study of the methanol adsorption on HZSM-5 zeolites by Mirth et al.[21] (cf. Figure 5 in ref 3 and Figure 2d in ref 21).

Conclusion

In conclusion we suggest five OH bands to be attributed to the water molecule complex with the bridging OH group in zeolites, at 3695, 3390, ~2900, ~2450, and ~1700 cm^{-1}. The 3390- and 3695-cm^{-1} bands belong to the water OH group interacting by two hydrogen bonds with the bridging OH group and with the nearest AlOSi bridging oxygen and to the other slightly perturbed water OH group, respectively. The broad pseudobands at ~2900, ~2450, and ~1700 cm^{-1} are the well-known (A, B, C) trio, typical for strong hydrogen-bonded complexes in vapors, liquids, and solids, being due to resonant interactions between the $\nu(OH)$ ± $k\nu(OH\cdots O)$ superposition modes and the $\delta(OH)$ and $\gamma(OH)$ overtones of the strongly perturbed bridging OH group.

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