

# The IR transmission windows of hydrogen bonded complexes in zeolites: A new interpretation of IR data of acetonitrile and water adsorption on zeolitic Brønsted sites

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## The IR transmission windows of hydrogen bonded complexes in zeolites: a new interpretation of IR data of acetonitrile and water adsorption on zeolitic Bronsted sites

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### ABSTRACT

The ~2800, ~2400 and ~1700 cm<sup>-1</sup> infrared OH bands recently found upon adsorption of many basic molecules on Bronsted sites of zeolites, including acetonitrile and water, are suggested to be analogous to the (A,B,C) triplet of medium-strong molecular X-OH·Y complexes in vapours, liquids and solids. IR studies of CD<sub>3</sub>CN and CCl<sub>3</sub>CN adsorptions on H-ZSM5, H-FeSil, H/D-ZSM5 and H/D-FeSil zeolites show these bands to be in a good agreement with the resonance theory of the (A,B,C) triplet, developed for molecular H-complexes. A new interpretation of IR data of water adsorption on zeolites, using this theory and results of ab initio calculations, suggests the water complex with the bridging OH group of zeolites to be "neutral", the one water OH group interacting by hydrogen bonds both with the bridging OH group and with the nearest AlOSi oxygen and the other OH group being free.

### INTRODUCTION

As found in recent IR studies of adsorption on zeolites [1-5], a wide range of H-complexes of basic molecules with zeolitic Bronsted sites show three broad OH bands with approximately constant position at ~2800, ~2400 and ~1700 cm<sup>-1</sup> (Table 1), very similar to the so-called (A,B,C) triplet [6-8] of medium-strong molecular X-OH·Y complexes in vapours, liquids and solids. Two alternative theories have been suggested to explain the origin of these bands for molecular H-complexes more than 20 years ago, the resonance and double-minimum theories. According to the resonance theory [6,7] these bands, actually pseudobands, are caused by subdivision of the very broad  $\nu(\text{OH}) \pm k\nu(\text{OH} \cdot \text{Y})$  superposition band by two Evans transmission windows at ~2600 and ~1900 cm<sup>-1</sup>, the  $\nu(\text{OH} \cdot \text{Y})$  being the intermolecular stretching mode. These transmission windows were supposed to result from strong Fermi resonance of the  $\nu(\text{OH}) \pm k\nu(\text{OH} \cdot \text{Y})$  combination modes with the  $2\delta(\text{OH})$  in-plane and  $2\gamma(\text{OH})$  out-of-plane overtones, the "missing" intensity being redistributed into adsorption regions on both sides of the windows by the resonance repulsion. As follows from a recent theoretical study of the (A,B,C) triplet for CsHSeO<sub>4</sub> crystals [9], in solids the C band can also be accounted for by a  $\delta(\text{OH}) + \nu(\text{TO})$  combination mode enhanced by the resonance with the  $\nu(\text{OH}) \pm k\nu(\text{OH} \cdot \text{Y})$  modes, the  $\nu(\text{OT})$  being a lattice vibration of the OH group oxygen.

Table 1  
(A,B,C) Triplet Wavenumbers<sup>a</sup> (cm<sup>-1</sup>)

adsorbed molecule	A	B	C <sup>b</sup>
acetonitrile	2890	2400	1780
water	2900	2500	1700
dimethylether	2950	2500	1900-1300
diethylether	2950	2300	1900-1300
di-n butylether	2900	2300	1900-1300
acetone	2900	2370	1800-1300
n-butylaldehyde	2900	2400	1700-1300
benzotrile	2800	2360	
formic acid	2900	2460	1700-1300
acetic acid	2900	2470	1800-1300

<sup>a</sup>From ref [2] with our assignment. <sup>b</sup>Apparently complicated by  $\delta(\text{OH}) + \nu(\text{TO})$  modes [1,9].

According to the double-minimum theory [9,10] the (A,B,C) triplet is produced by a pair of quasigenerate vibrational levels of an asymmetric double-minimum proton potential, corresponding to the "neutral" X-OH·Y and "ionic" X-O<sup>-</sup>·HY<sup>+</sup> states of H-complexes. Considering the proton tunnelling through the potential barrier between two minima, the selection rules for transitions amongst the lowest levels in such a potential permit four of the infrared active type. As the separation between the corresponding OH bands and their intensity depend on the exact shape of the potential, only three or fewer bands may be observable under certain circumstances [10]. Although, from the physical point of view, neither the resonance theory nor the double-minimum theory have been rigorously proved for a concrete case of the (A,B,C) triplet yet, the former one appears to be the most likely of them now. One of the most convincing reasons for this is its good qualitative agreement with some interesting regularities of change of the A+B+C band on strengthening the acid-base interaction [6,7], which could not be explained by the double-minimum theory. First of all this concerns the roughly constant position of the A, B and C bands and the behavior of their comparative intensities on going from medium-strong "neutral" X-OH·Y via strong quasisymmetric X-O·H·Y to very strong "ionic" X-O<sup>-</sup>·Y complexes (see [6,7] for more details).

An experimental proof of the analogy between the ~2800, ~2400 and ~1700 cm<sup>-1</sup> bands of surface H-complexes and the (A,B,C) triplet of molecular H-complexes is very important from two points of view. First, this should justify the application of the well-developed resonance theory to the interpretation of numerous IR data on surface acid-base interactions, related to the topical problem of proton-transfer reactions in the theory of heterogeneous catalysis. Second, from methodological point of view, the study of the nature of the (A,B,C) triplet can be more convenient for surface H-complexes than for H-complexes in vapours, liquids and solids. IR spectra for surface H-complex are not complicated by vibrational-rotational transitions, like for vapours. At the same time, the interaction with media can be neglected for surface H-complexes, as distinct from H-complexes in liquids and solids.

As shown in our recent IR and ab initio studies [1], the ~2900, ~2400 and ~1700 cm<sup>-1</sup> OH bands in CD<sub>3</sub>CN adsorption on the bridging OH groups of zeolites are associated with only one "neutral" H-complex with single-minimum proton potential,

in contradiction to the double-minimum theory. In the present paper a direct proof will be given for the first time in the study of the (A,B,C) triplet, using  $\text{CD}_3\text{CN}$  and  $\text{CCl}_3\text{CN}$  adsorptions on deuterated H-ZSM5 and H-FeSil zeolites, that the transition window minimum between the A and B bands of the D-complexes corresponds exactly to the  $2\delta(\text{OD})$  in-plane bending overtone frequency of the perturbed OD group. This verifies the resonance theory of the A and B bands. A revision of IR data on water complexes with the bridging OH group of zeolites, using the resonance theory and results of ab initio calculations, will show this complex to be "neutral", in contradiction with the generally accepted suggestion [3,4,5,11,12] that water molecule is protonated in this interaction.

Considering numerous experimental IR studies of H-complexes in zeolites during the last 50 years, a modern reconsideration of these IR data on the basis of the resonance theory can lead to a significant revision of many other previously accepted mechanisms associated with the proton acidity of zeolites.

## EXPERIMENTAL SECTION

ZSM5 (Si/Al=52) was synthesized hydrothermally at 440 K for 48 h with TPA Br as the templating agent. The ferrosilicate FeSil (Si/Fe=32) was prepared using iron sulfate and silicate solution. Deuteration of H-ZSM5 and H-FeSil was performed by reacting the activated samples for 1.5 h at 623 K with 100 mbar of  $\text{D}_2$ .

IR spectra were recorded at room temperature using a Bruker IFS 113v FTIR spectrometer with a heatable vacuum cell. Before gas dosage the samples were activated for 1 h at 723 K in high vacuum.

## THEORETICAL SECTION

Ab initio calculations of molecular models were performed at the SCF 6-31G\* level using the GAUSSIAN-90 package.

## RESULTS AND DISCUSSION

### 1. $\text{CD}_3\text{CN}$ and $\text{CCl}_3\text{CN}$ adsorptions on H-ZSM5, H-FeSil, H/D-ZSM5 and H/D-FeSil

As shown in [13], H $\rightarrow$ D exchange of H-zeolites gives rise to infrared observable  $\delta(\text{OD})$  bands of the bridging OD groups, between the bands of symmetric ( $600\text{-}800\text{ cm}^{-1}$ ) and asymmetric ( $1000\text{-}1300\text{ cm}^{-1}$ ) lattice T-O vibrations. Figure 1 and Table 2 show the changes in this spectral range for  $\text{CD}_3\text{CN}$  and  $\text{CCl}_3\text{CN}$  adsorptions on H/D-ZSM5 and H/D-FeSil zeolites. Both the upward shift values of  $65\text{-}95\text{ cm}^{-1}$  and approximately the same band intensities with and without the interaction are in agreement with experimental IR studies of the in-plane bending vibrations for

Table 2  
 $\delta(\text{OD})$  Band and Transmission Window Minimum Wavenumbers ( $\text{cm}^{-1}$ ).

Bronsted site	$\delta(\text{OD})$	$\text{CD}_3\text{CN}$ adsorption			$\text{CCl}_3\text{CN}$ adsorption	
		$\delta(\text{OD})$	shift	window	$\delta(\text{OD})$	shift
SiODAl	894	988	94	1977	970	76
SiODFe	865	950	85	1902	930	65

Table 3  
A and B Band Positions ( $\text{cm}^{-1}$ )

Bronsted site	$\text{CD}_3\text{CN}$ adsorption			$\text{CCl}_3\text{CN}$ adsorption		
	A	B	(A,B) <sup>a</sup>	A	B	(A,B) <sup>a</sup>
SiOHA1	2770	2400	~2500	2945	2520	~2800
SiOHFe	2810	2385	~2600	3000	2430	~2900
SiODAl	2060	1875		2230		
SiODFe	2130	1860		2270		

<sup>a</sup>The center of gravity [7] corresponds to the crossing point of the  $\nu$  axis and the vertical line dividing the (A,B) area into two subareas of approximately equal integral intensity.

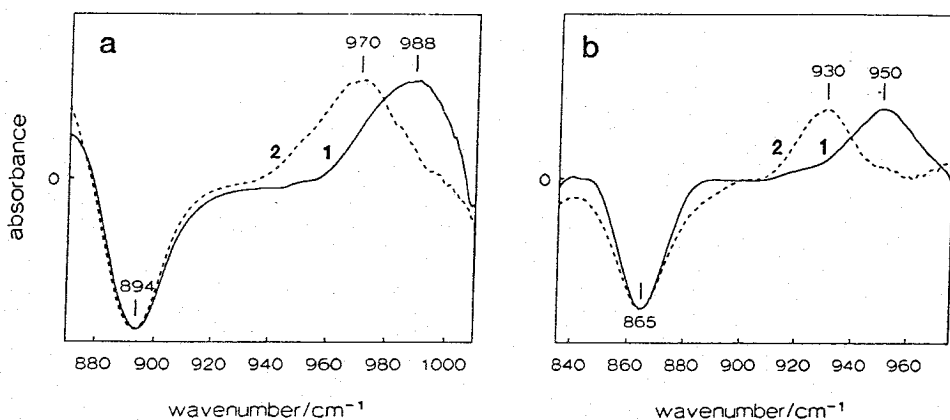


Figure 1. Changes in the spectral ranges of the  $\delta(\text{OD})$  vibrations of (a) H/D-ZSM5 induced by  $\text{CD}_3\text{CN}$  (1) and  $\text{CCl}_3\text{CN}$  (2) adsorptions at 295 K and 0.05 mbar; (b) H/D-FeSil induced by  $\text{CD}_3\text{CN}$  adsorption at 295 K and 0.05 mbar (1) and  $\text{CCl}_3\text{CN}$  adsorption at 295 K and 1.36 mbar (2).

molecular H-complexes [14].

Figure 2 shows the  $1300\text{--}4000\text{ cm}^{-1}$  spectral range of H-ZSM5 and H/D-ZSM5 with adsorbed  $\text{CD}_3\text{CN}$  and  $\text{CCl}_3\text{CN}$ , the band maxima being reported in Table 3. On going from H-ZSM5 to H/D-ZSM5 the intensities of the A and B bands of the perturbed SiOHA1 groups decrease, while the broad and complex bands of the perturbed SiODAl groups appear in the  $1800\text{--}2200\text{ cm}^{-1}$  range. The similar effect takes place for the adsorptions on H-FeSil and H/D-FeSil (see Table 3, the spectra are not reported). In agreement with the resonant theory for medium-strong "neutral" H-complexes [6,7], the center of gravity of the (A,B) OH doublet shifts to higher frequencies on going from  $\text{CD}_3\text{CN}$  to  $\text{CCl}_3\text{CN}$  and from SiODAl to SiODFe (see Table 3), due to the lower basicity of  $\text{CCl}_3\text{CN}$  compared with  $\text{CD}_3\text{CN}$  and the lower acidity of SiODFe compared with SiODAl.

Neither the OH nor the OD bands can be directly used to check whether the Evans window positions correspond to the in-plane bending overtones. For the perturbed

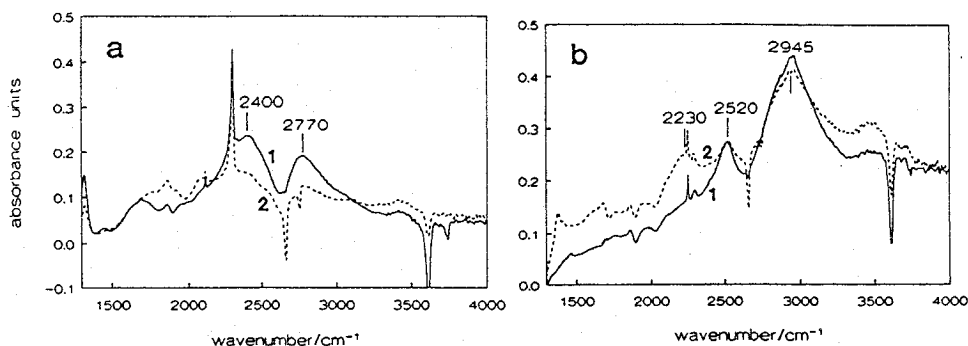


Figure 2. Changes in the 1500-4000  $\text{cm}^{-1}$  range of (a) H-ZSM5 (1) and H/D-ZSM5 (2) induced by  $\text{CD}_3\text{CN}$  adsorption at 295 K and 0.05 mbar; (b) H-ZSM5 (1) and H/D-ZSM5 (2) induced by  $\text{CCl}_3\text{CN}$  adsorption at 295 K and 0.05 mbar.

$\text{SiOHAl}$  and  $\text{SiOHFe}$  groups Evans windows are well pronounced in the  $\nu(\text{OH}) \pm \nu(\text{OH} \cdot \text{CD}_3\text{CN})$  and  $\nu(\text{OH}) \pm \nu(\text{OH} \cdot \text{CCl}_3\text{CN})$  bands at  $\sim 2600 \text{ cm}^{-1}$  (Figure 2), but the  $\delta(\text{OH})$  in-plane bending bands are obscured by the asymmetric lattice vibrations in the 1000-1300  $\text{cm}^{-1}$  range. For the perturbed  $\text{SiODAl}$  and  $\text{SiODFe}$  groups the  $\delta(\text{OD})$  bands are observable (Figure 1), but the 1800-2000  $\text{cm}^{-1}$  range, where the Evans windows are expected to be, according to the  $\delta(\text{OD})$  frequencies (Table 2), is strongly complicated by two sharp lattice bands at 1880 and 2007  $\text{cm}^{-1}$  (see, for example, [15]). Also in the difference spectra this range remains very complex as the subtraction of the intense 1880 and 2007  $\text{cm}^{-1}$  bands of unloaded zeolites from these slightly shifted by the adsorption produces "imaginary" positive (at  $\sim 1860$  and  $\sim 1970 \text{ cm}^{-1}$ ) and negative ( $\sim 1895$  and  $\sim 2030 \text{ cm}^{-1}$ ) bands (see Figure 2). This makes an unambiguous interpretation of the real OD bands hardly possible.

The spectra recorded after the adsorptions on the H/D- and H-forms of zeolites in the 1800-2000  $\text{cm}^{-1}$  range (Figure 2), can be written, respectively, as

$$S^d = S_{\text{OD}}^d + S_{\text{L}}^d + S_{\text{OH}}^d \quad (1)$$

and

$$S^h = S_{\text{OH}}^h + S_{\text{L}}^h \quad (2)$$

$S_{\text{OD}}$ ,  $S_{\text{OH}}$  and  $S_{\text{L}}$  designating the OD, OH and lattice 1880 and 2007  $\text{cm}^{-1}$  bands. Assuming the lattice vibrations to be independent on the H $\rightarrow$ D exchange, that means

$$S_{\text{L}}^d = S_{\text{L}}^h \quad (3)$$

$S_{\text{OD}}^d$  can be written as

$$S_{\text{OD}}^d = (S^d - S^h) - (S_{\text{OH}}^d - S_{\text{OH}}^h) \quad (4)$$

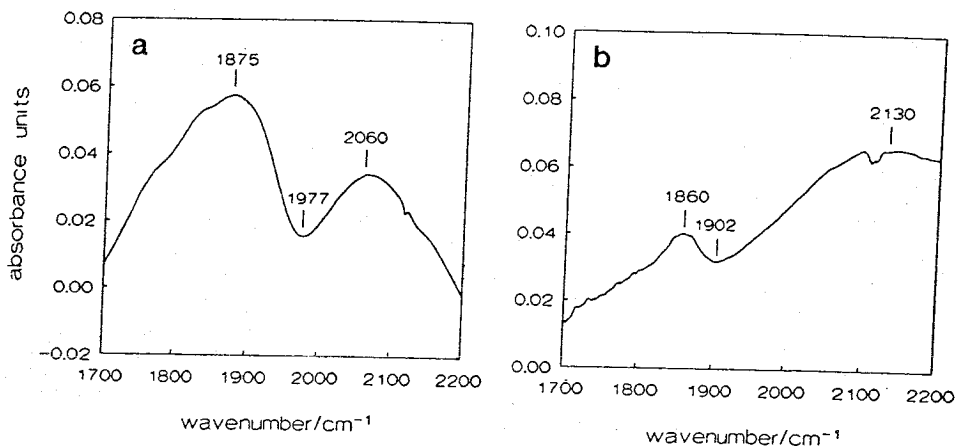


Figure 3. The  $S_{OD}^d$  spectra of (a) H/D-ZSM5 induced by  $CD_3CN$  adsorption at 295 K and 0.05 mbar; (b) H/D-FeSil induced by  $CD_3CN$  adsorption at 295 K and 0.05 mbar.

As  $S_{OH}^d$  and  $S_{OH}^h$  are smooth low-frequency tails of the OH bands in the 1800-2000  $cm^{-1}$  range (Figure 2), the term  $(S_{OH}^d - S_{OH}^h)$  can be neglected in (4), being capable of changing only the base-line of the  $S_{OD}^d$  spectra. In Figure 3 the  $S_{OD}^d$  curves are presented for the  $CD_3CN$  adsorption on H-ZSM5 and H/D-FeSil, constructed as

$$S_{OD}^d = (S^d - S^h) \quad (5)$$

The transmission windows become well pronounced in these spectra with the minima at 1977 and 1902  $cm^{-1}$ , very close to their expected values of  $2 \times 988 = 1976$  and  $2 \times 950 = 1900$   $cm^{-1}$  (see Table 1). Verifying the resonance theory of the (A,B) doublet, this implies the  $\sim 2800$ ,  $\sim 2400$  and  $\sim 1700$   $cm^{-1}$  bands found in adsorption of many basic molecules on zeolites, to be pseudobands caused by Fermi resonance between the  $\nu(OH) \pm k\nu(OH \cdot Y)$  combination modes and the  $2\delta(OH)$  overtone of the perturbed bridging OH group.

## 2. Water adsorption on the bridging OH group of zeolites

The conclusion of experimental IR studies [3,4,5] in favour of the  $H_3O^+$  ion formation in water adsorption on zeolites 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  $H_3O^+$ . However, according to the resonance theory these two bands are associated with the  $\nu(OH) \pm k\nu(OH \cdot Y)$  modes of the perturbed bridging OH group, implying the water molecule to be "neutral" in this interaction. Owing to the difficulties of discriminating between the "neutral" and "ionic" structures on the basis of energy calculations (see [11] for more details), a theoretical support for the "neutral" structure will be based on the OH frequency calculations.

To demonstrate the reliability of the adopted approximation, in Table 4 the

Table 4  
OH Frequency Shifts<sup>a</sup> (cm<sup>-1</sup>)

structure	assignment	calcd	obsd <sup>b</sup>
1	$\nu(\text{OH}_{\text{nb}})$	24	20
	$\nu(\text{OH}_{\text{b}})$	-136	-171

<sup>a</sup>With respect to the uncoupled O-H vibrator frequency of HOD molecule. <sup>b</sup>Ref 16.

Table 5: OH Frequency Shifts<sup>a</sup> (cm<sup>-1</sup>)

assignment	calcd		obsd <sup>b</sup>
	2	3	
$\Delta\nu(\text{OH}_{\text{nb}})$		43	
$\Delta\nu(\text{OH}_{\text{wb}})$	4		8
$\Delta\nu(\text{OH}_{\text{b}})$	-273	-248	-297

<sup>a</sup>With respect to the uncoupled O-H vibrator frequency of HOD molecule. <sup>b</sup>The 3695 and 3390 cm<sup>-1</sup> frequency [4,5] shifts.

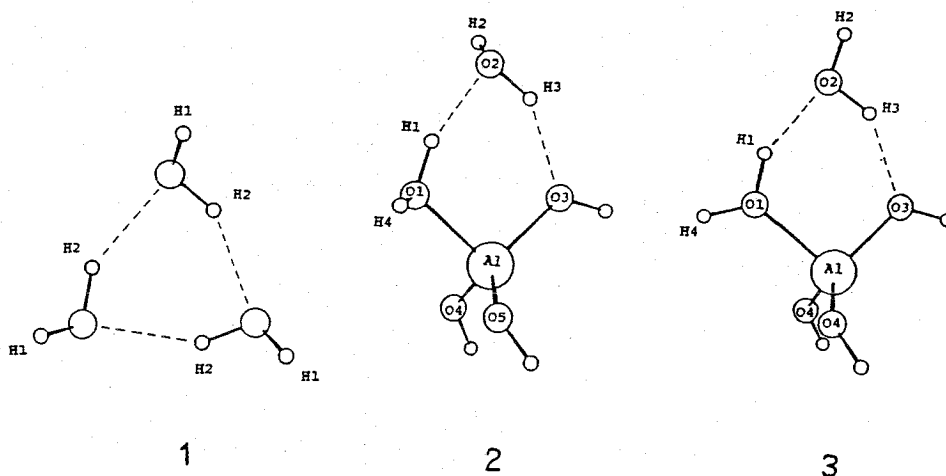


Figure 4. Molecular models.

calculated and experimental [16] OH frequency shifts of the water trimer are presented, with each water molecule interacting by means of two hydrogen bonds (Figure 4). As the coupling between the nonbonded and bonded O-H vibrators in the complex is quite small, their  $\nu_{\text{nb}}$  and  $\nu_{\text{b}}$  shifts with respect to the uncoupled water O-H vibrator frequency  $\nu^0(\text{OH})$  are used, being the most appropriate of the OH vibration characteristics [17] for water structure analysis in complex hydrogen-bonded aggregates. The  $\nu^0(\text{OH})$  is taken to be the HOD  $\nu(\text{OH})$ , the experimental and 6-31G\* values being 3687 [16] and 4131 cm<sup>-1</sup>.



The full optimization of the water position with respect to the  $\text{H}_2\text{O}\cdot\text{Al}(\text{OH})_4$  molecular analog of the bridging OH group leads to structure 2 (Figure 4) which is in a good agreement with the experimental OH frequency shifts (Table 5). As distinct from structure 3 optimized with the  $C_s$  symmetry constraint, in 2 the  $\text{O}^2\text{-H}^2$  bond is strongly shifted from the  $\text{O}^1\text{O}^2\text{O}^3$  plane and slightly weakened. Structure 3, with the  $\text{O}^2\text{-H}^2$  vibrator being nonbonded, overestimates the highest OH frequency of the adsorbed water significantly (Table 5). We consider structure 2 to be a molecular analog for the water adsorption on the bridging OH group of zeolites, with the  $\text{O-H}_b$  and  $\text{O-H}_{wb}$  (weakly bonded) vibrators being responsible for the strongly and slightly shifted 3390 and 3695  $\text{cm}^{-1}$  frequencies [4,5], with respect to  $\nu^0(\text{OH})$ .

## CONCLUSION

In conclusion we suggest five OH bands to be attributed to the water complex with the bridging OH group in H-ZSM5 zeolites, at 3695, 3390, ~2900, ~2400 and ~1700  $\text{cm}^{-1}$ . The 3390 and 3695  $\text{cm}^{-1}$  bands belong to the water OH group interacting by two hydrogen bonds with the bridging OH group and with the nearest  $\text{AlOSi}$  bridging oxygen and to the other slightly perturbed water OH group, respectively. The broad bands at ~2900, ~2450 and ~1700  $\text{cm}^{-1}$  are analogous with the (A,B,C) triplet of medium-strong molecular H-complexes, interpreted by the resonance theory.

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