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IR spectroscopic study of the adsorption of MeOH and H_2O on decationized zeolites

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The IR spectra of decationized zeolites with adsorbed bases have been analyzed. A correlation between the shift $\Delta\nu$(OH) of the center of gravity of the set of bands *A*, *B*, and *C* (components of the ν(OH) vibration) and the strength of the H-bond between the bridging hydroxyl groups and the molecule of a base has been found. This is evidence in support of the Fermi-resonance nature of the perturbations of the ν(OH) vibration. Spectral data on the adsorption of H_2O and MeOH on decationized zeolites that cannot be interpreted in terms of the formation of complexes with strong H-bonds have been obtained. Arguments in favor of the formation of H_3O^+ and $MeOH_2^+$ ions linked to the neighboring oxygen atoms in the zeolite lattice *via* two identical hydrogen bridges have been presented.

Key words: decationized zeolites; adsorption; IR spectra.

Previously[1] an attempt was made to consider IR-spectroscopic data on the adsorption of weak bases and of bases of medium strengths on zeolites in terms of the formation of strong H-bonds between the acidic OH groups of zeolites and the molecules being adsorbed. These bonds are characterized by broad absorption bands with maxima at 2900, 2400, and 1700 cm^{-1} (bands *A*, *B*, and *C*, respectively).[2] The appearance of these bonds in the IR spectra is probably due to strong Fermi resonance between the stretching vibrations and the first overtones of the in-plane and out-of-plane bending vibrations of the OH group.[3] Bands *A*, *B*, and *C* are typical of the spectra of crystals of acid salts with a two-well potential function for the proton.[4,5] These bands have been observed for the adsorption of diethyl ether (DEE) on fojazites containing Nd^{3+} ions, and bands *A* and *B* were also detected in the IR spectra of H—Na—Y zeolite after adsorption of DEE and acetone.[6,7]

However the participation of the acidic OH groups of zeolites in the formation of strong H-bonds during the adsorption of weak bases (H_2O, MeOH) is doubtful. In fact, an estimate of the length of the *r*(O...O) H-bond, carried out by us on the basis of its parameters found previously[1] by a nonempirical calculation of the $H_2O...HO(AlO_3H_4)$ adsorption complex, affords a value of 2.67 Å. Such an H-bond is not strong, and bands *A*, *B*, and *C* are exhibited in the IR spectra of compounds containing H-bonds whose lengths are no more than 2.55 Å.[4,8]

In view of the fact that the possibility of protonation of bases like H_2O and MeOH had been shown previously,[9—13] it was of interest to see whether H_3O^+ and $MeOH_2^+$ ions can react with the oxygen atoms in the lattice of H—Na—Y zeolites to give strong H-bonds.

Experimental

The NH_4—Y zeolites of compositions $0.7(NH_4)_2O \cdot 0.25Na_2O \cdot Al_2O_3 \cdot 5.08SiO_2 \cdot 8.03H_2O$ and $0.85(NH_4)_2O \cdot 0.09Na_2O \cdot Al_2O_3 \cdot 3.34SiO_2 \cdot 5.59H_2O$ were obtained by treating Na—Y* zeolites with an aqueous solution of ammonium hydroxide. Samples for recording IR spectra were prepared by compacting the powders under a pressure of $3 \cdot 10^3$ kG cm^{-2}. The pressed pellets were deammoniated and dehydrated by heating *in vacuo* at 350—400 °C. The final pressure was 10^{-5}—10^{-6} Torr. IR spectra were recorded at room temperature on a UR-20 spectrophotometer.

Results and Discussion

Strong H-bonds are usually clearly manifested in the region of stretching vibrations of OH groups (Fig. 1). Curve *1* shows the spectrum of H—Na—X zeolite containing adsorbed DEE after elimination of the absorption bands corresponding to the adsorbate and to the aluminosilicate framework. The positions and shapes of the *A*, *B*, and *C* bands in this spectrum are similar to those in the spectrum of the acid silicate $NaCaHSiO_4$ (curve *2*), in which the length of the H-bonds between the $[O_3SiOH]^{3-}$ anions amounts to ~2.5 Å.[14]

It has been shown in relation to complexes of carboxylic acids with organic bases[15] that, as the H-bonds in these complexes become stronger, the center of gravity of the *A*, *B*, and *C* set of bands is gradually displaced to the low-frequency region. When the H-bonds are very strong ($-\Delta H >$ 11 kcal mol^{-1}), this shift may result not only in a redistribution of the intensities of bands *A*,

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* Na—Y zeolites were synthesized by N. N. Feoktistova.

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Table 1. Stretching vibrations of bridging OH groups involved in the formation of strong H bonds with molecules of bases

Base	*PA** /kJ mol^{-1}	Zeolite	ν(OH)/cm^{-1}			Reference
			A	*B*	*C*	
Acetonitrile	788	H—X	2995 vs	—	—	18
		H—Y	2800 s	2400 m	—	19
		H—ZSM-5	2770 s	2405 vs	1700 vw	18
Dimethyl ether	804	H—ZSM-5	2950 m	2400 w	1900—1300 s	17
Acetone	823	H—Y	2800 m	2450 m	1600—1300 w	18
		H—ZSM-5	2820 w	2370 m	1600—1300 s	18
Diethyl ether	838	H—Nd—X	2800 s	2400 s	1740 s	6
		H—Ce—Y	2800 s	2410 s	1700 s	6
		H—ZSM-5	2950	2300	1900—1300	17
Tetrahydrofuran	831	H—ZSM-5	—	2370	1900—1300	17
Diisopropyl ether	862	H—ZSM-5	—	—	1900—1300	17

* The proton affinities for bases in the gas phase were taken from Ref. 17.

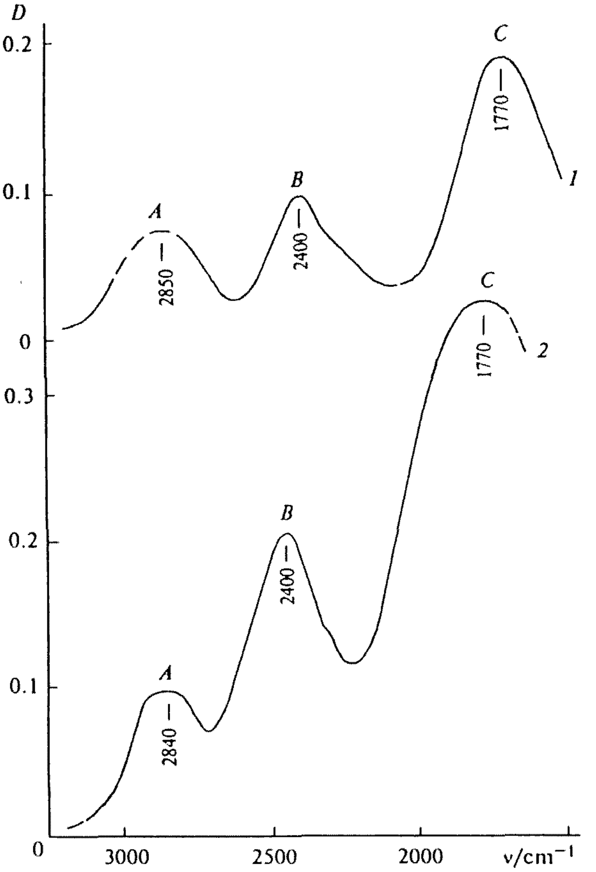


Fig. 1. Sets of three bands for the stretching OH vibrations (*A*, *B*, *C*) in systems with strong hydrogen bonds: the bridging hydroxyl—diethyl ether associates in Nd—Na—X zeolite (*1*); curve *1* corresponds to the difference between the IR spectra of the zeolite with adsorbed ether and of the activated zeolite; H-bound associates in the structure of the acidic silicate $NaCaHSiO_4$ (*2*); curve *2* is the IR spectrum of $NaCaHSiO_4$ powder pressed with KBr.

B, and *C*, but also in the appearance of new bands *D* and *E* with maxima at 1100 and 850 cm^{-1}, respectively.[16]

The trend of the center of gravity of the bands to shift to lower frequencies as the strength of the H-bond increases can be followed rather clearly when bases of moderate strengths are adsorbed on zeolites with Brønsted acidic centers (Table 1). To estimate the relative basicities of organic molecules (see Ref. 17), one can use the values of the proton affinity of these molecules in the gas phase (*PA*, kJ mol^{-1}). The smallest shift Δν(OH) with respect to the frequency corresponding to unbound acidic hydroxyls (600—1000 cm^{-1}) is observed in the case of acetonitrile (*PA* = 788 kJ mol^{-1}). The spectra of H—Y and H—ZSM-5 zeolites exhibit practically no absorption in the 1900—1300 cm^{-1} region that could be attributed to band *C*, while the spectrum of H—X zeolite contains neither band *C* nor band *B*. In the latter case, only one broad ν(OH) band with a maximum at 2995 cm^{-1} is observed, while the very weak and narrow band at 2435 cm^{-1} (see Ref. 18) apparently corresponds to an overtone of the in-plane bending vibrations [2δ(OH)], whose intensity is increased due to Fermi resonance.

In the case of adsorption of dimethyl and diethyl ethers and acetone (*PA* = 804 to 838 kJ mol^{-1}), all three absorption bands are observed, and the intensities of bands *C* are similar to those of bands *A* and *B* or even exceed them. On going to tetrahydrofuran, band *A* disappears, and in the case of diisopropyl ether (*PA* = 862 kJ mol^{-1}), only band *C* is retained. Thus, the center of gravity of the bands shifts substantially to the low-frequency region, and one might expect that bands *D* and *E* would appear in the spectrum, although they would be very difficult to detect due to the strong absorption of the zeolite lattice.

The shift Δν(OH) of the center of gravity of bands *A*, *B*, and *C* to lower frequencies that occurs as the strength

Table 2. Stretching and bending vibrations of oxonium and methoxonium ions in zeolites

Base	Zeolite	ν(OH)/cm^{-1}		δ(HOH)*/cm^{-1}	Reference
H_2O	H—ZSM-5	3695 s, sr**	2885 s, br, 2457 s, br	1630 s, sr	9
	H—ZSM-5	3700 s, sr	2900 s, br, 2470 s, br	1620 m, sr	21
	H—SAPO-34	3678 s, sr	2890 m, br	1610 m, sr	10
		3570 w, sr	2600 sh, 2475 s, br		
	H—Y	3710 m, sr	3000 m, br, 2515 m, br	1632 m, sr	22
MeOH	H—ZSM-5	3545 vs, sr	2900 w, br, 2440 m, br	1687 s, sr	11
	H-mordenite	3525	2900, 2410	1740	13
	H-erionite	—	2950 s, br	1645 m, sr	12
			2450 m, br	1505 m, sr	
	H—Na—Y	—	2900 s, br, 2430 s, br	1740 m, sr	13

Note. These spectra correspond to a coverage of 1 molecule of adsorbate per zeolite H-site. The adsorption of bases was carried out at room temperature (*cf.* Refs. 21, 22: at 80 °C).

* Bending vibration of the OH_2^+ group (see the text); in the case of H_3O^+, the δ(HOH) frequency is close to $\nu_4(E)$ for an ion with C_{3v} symmetry. ** sr — Means a sharp form of the band.

of the H-bond between the bridging hydroxyl and the molecule of a base increases is evidence, as in the case of complexes of carboxylic acids with organic bases,[16,20] for the Fermi-resonance nature of the perturbations of the broad ν(OH) band leading to its splitting into the *A*, *B*, and *C* components.

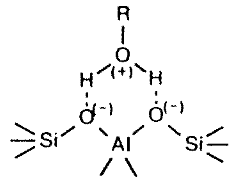
Evidently, the strengths of H-bonds depend on more than just the proton affinity of the bases. The sizes and geometries of adsorbate molecules largely determine the character of their localization in cavities and channels of the zeolites, and, consequently, the interatomic distances in adsorption complexes. For example, although the *PA* of NH_3 and of dibutyl ether are practically identical (853 and 852 kJ mol^{-1}, respectively), the latter is adsorbed on H—ZSM-5 zeolite forming a strong H-bond characterized by *A*, *B*, and *C* bands,[17] whereas NH_3, like stronger bases (*n*-propylamine, *PA* = 912 kJ mol^{-1}, pyridine, 924 kJ mol^{-1} *etc.*), is protonated on all zeolites containing acidic centers.

When weak bases are adsorbed, only relatively small shifts of the bands for the stretching OH vibrations to lower frequencies are observed in the IR spectra, but no splitting occurs. In fact, in the case of the adsorption of ethylene (*PA* = 680 kJ mol^{-1}), benzene (759 kJ mol^{-1}), and even toluene (794 kJ mol^{-1}) on H—Na—Y and H—ZSM-5 zeolites, these shifts amount to 280—410 cm^{-1} (see, for example, Ref. 17). Molecules of these bases interact with the H-centers of the zeolite through the π-electrons of the C=C double bond or of the benzene ring. This interaction is much weaker than the H-bonds between the H-centers and bases containing O and N atoms with unshared electron pairs (see Table 1).

Due to their low proton affinities, H_2O (697 kJ mol^{-1}) and MeOH (761 kJ mol^{-1}) molecules apparently cannot participate in the formation of strong H-bonds with the Si(OH)Al acidic groups of zeolites. Therefore, the appearance of the whole triad of bands *A*, *B*, and *C* in the IR spectra, as has been suggested previously,[1] is relatively unlikely. It can be seen from Fig. 1 that for complexes with strong H-bonds these bands are similar in their widths. In the case where H_2O and MeOH are adsorbed on zeolites, pairs of broad bands in the 2400—3000 cm^{-1} region and narrow bands in the 1600—1630 cm^{-1} (H_2O) and 1500—1750 cm^{-1} (MeOH) ranges arise in the spectra (Table 2).

The frequencies of the broad bands for H_2O and MeOH are virtually identical (see Table 2) and almost do not change as the Si/Al ratio in the zeolites increases, although the acidity of the bridging OH groups increases, and the strength of the corresponding H-bonds should also increase. On the other hand, the positions of the narrow bands recorded in the 1500—1750 cm^{-1} range in the spectra of methanol adsorbed on various zeolites are markedly dissimilar, and in the case where erionite is taken as the adsorbent, these bands have more than one maximum. Finally, as has been found previously,[11] when MeOH is adsorbed on H—ZSM-5 zeolite, the intensities of the bands in the 2400—3000 cm^{-1} region dramatically decrease at coverages of more than one molecule per acidic center. At the same time, the intensity of the narrow band at 1687 cm^{-1} increases, and this band itself shifts to 1620—1580 cm^{-1}. Thus, the spectra characterizing the adsorption of H_2O and MeOH on decationized zeolites possess some specific features that are at variance with the concept of the formation of complexes containing strong H-bonds.

At the same time, the two broad bands in the 2400—3000 cm^{-1} range can be assigned to the symmetrical [ν_s(OH)] and antisymmetrical [ν_{as}(OH)] stretching vibrations of hydroxonium and methoxonium ions, and the narrow bands at 1500—1750 cm^{-1} may be due to the deformation vibrations of the same ions.[9—13] The previously suggested[11,13] two-center scheme for the adsorption complex seems to be the most likely.



(I)

where R = H or Me.

This scheme is in good agreement with the results of *ab initio* quantum-chemical calculations of the energies of proton transfer and of the enthalpies of adsorption of H_2O and MeOH for clusters serving as models of the proton acidic centers of zeolites.[23]

According to Scheme (I), the similarity of the spectra of zeolites with adsorbed H_2O and MeOH in the region of stretching OH vibrations is readily explained by the similarity of the configurations of the OH_2^+ groups incorporated in the H_3O^+ and $MeOH_2^+$ ions, which form two identical H-bonds with the neighboring $O^{(-)}$ atoms in the zeolite lattice. The $\Delta\nu(OH) = \nu_s(OH) - \nu_{as}(OH)$ splitting is 415—485 cm^{-1} for H_3O^+ and 460—500 cm^{-1} for $MeOH_2^+$. The displacement of the center of gravity of the $\Delta\nu_s(OH)$ and $\nu_{as}(OH)$ bands to lower frequencies by approximately 1000 cm^{-1} with respect to the bands for the free ions makes it possible to classify these H-bonds as moderately strong. This conclusion is in agreement with the high densities of hydroxonium and methoxonium ions and with the high proton-accepting ability of the $O^{(-)}$ atoms in the zeolite.

The narrow $\nu(OH)$ band observed in the 3678—3710 cm^{-1} range in the spectrum of adsorbed water (see Table 2) corresponds to the stretching vibration of the free O—H bond in the H_3O^+ ion. According to Scheme (I), the spectrum of adsorbed methanol should not contain a similar high-frequency band, and this is actually the case for H—Y zeolite and for H-erionite. However, the spectra of zeolites with higher Si/Al ratios exhibit narrow intense bands at 3545 cm^{-1} (H—ZSM-5) and 3525 cm^{-1} (H-mordenite). These bands (see Refs. 11 and 13) can be assigned to the free OH-groups in the $MeOH_2^+$ ions, whose hydrocarbon units are directed at the lattice of highly-siliceous zeolites.

When the number of MeOH or H_2O molecules in the channels of H—ZSM-5 zeolite or H-mordenite is approximately equal to the number of proton centers in these zeolites, the IR spectra exhibit only absorption bands for methoxonium and hydroxonium ions (see Table 2). When adsorption is carried out on zeolites with lower proportions of silica (H-erionite and especially H—Na—Y), additional bands in the 3200—3600 cm^{-1} range are observed in the spectra recorded at the same coverages; these bands can be assigned to vibrations of the lattice OH groups, perturbed by the hydrogen bonds with the adsorbate molecules. It is seen from Fig. 2 (curve *2*) that the spectrum of H—Na—Y zeolite at low coverages with MeOH (<6 molecules per unit cell) has, along with the bands at 2970, 2500, 1720, and 1675 cm^{-1} corresponding to the methoxonium ions, bands of medium intensity at 3300 and 3450 cm^{-1}, which can be attributed to the Si(OH)Al and SiOH groups, respectively, incorporated in the H-bonds with the oxygen atoms of MeOH molecules. The vibrations of the free OH bonds in methanol are manifested in the spectrum as a weak band at 3490 cm^{-1}.

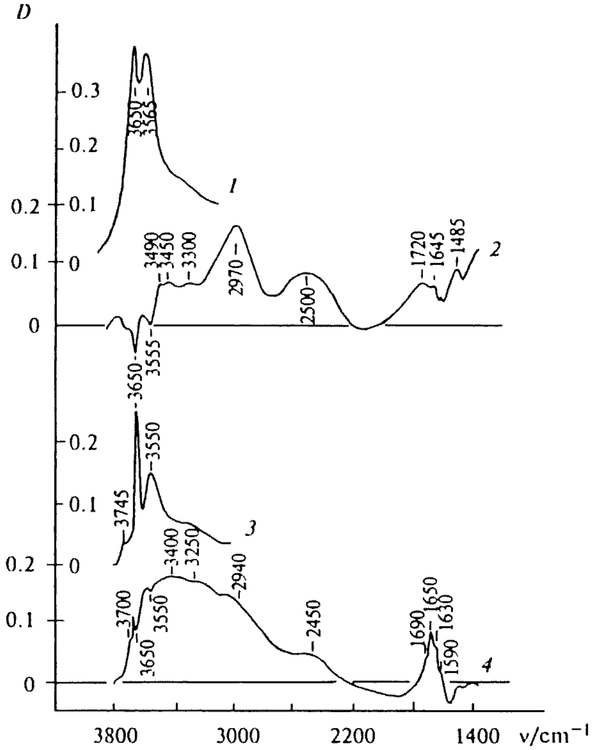
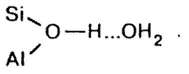


Fig. 2. Interaction of bridging hydroxyls of H—Na—Y zeolites with methanol and water molecules: IR spectrum of NH_4—Y zeolite (Si/Al = 2.6) heated for 3 h *in vacuo* at 400 °C (*1*); difference between the IR spectra of zeolite recorded in the presence and in the absence of adsorbed MeOH (*2*); IR spectrum of NH_4—Y zeolite (Si/Al = 1.66) heated for 2 h *in vacuo* at 360 °C (*3*); difference between the IR spectra of zeolite with adsorbed H_2O and activated zeolite (*4*).

When H_2O is adsorbed on H—Na—Y zeolite, the number of H_3O^+ ions formed is fairly small compared to the overall number of adsorbed molecules. It can be seen from Fig. 2 (curve *4*) that the weak bands corresponding to H_3O^+ ions at 2940 and 2450 cm^{-1} are exhibited on the low-frequency slope of the wide band corresponding to $\nu(OH)$ of the H_2O molecules. The inflection (shoulder) at 3700 cm^{-1} on the high-frequency slope of the same band corresponds to vibrations of the free OH-bonds in the H_3O^+ ions. The complex structure of the $\delta(HOH)$ band, which consists of a set of narrow bands, indicates that the adsorbed water molecules can exist in states other than H_3O^+ ions.

The ratio of the integral intensities of the "negative" $\nu(OH)$ bands at 3650 and 3550 cm^{-1} (see Fig. 2, curve *4*) to the intensities of the corresponding bands in the spectrum of the initial zeolite (curve *3*) indicates that approximately 20 % of the bridging OH groups have reacted with water molecules; the majority of these groups were the OH groups manifested at a frequency of 3650 cm^{-1}. It follows from the ratio of the total integral intensity of the bands at 2940 and 2450 cm^{-1} corresponding to H_3O^+ ions to the integral intensity of the band for water molecules in the 3800—2000 cm^{-1} range that no more than one group of 10 bridging OH groups that have reacted is involved in the protonation of water molecules, while the rest of these groups form hydrogen bonds with water:



According to Scheme (1), as the numbers of adsorbed H_2O and MeOH molecules increase, the difference between the processes of the formation of water and methanol clusters from H_3O^+ and $MeOH_2^+$ ions should become more pronounced. Whereas the oxonium ion readily forms an H-bond with a water molecule *via* its free OH group, in the case of the methoxonium ion, cleavage of one of its H-bonds with the zeolite lattice is needed, and this is accompanied by substantial corresponding changes in its IR spectrum. In fact, this difference can be observed by comparing the results of the IR-spectroscopy studies of the adsorption of water[9] and methanol[11] on H—ZSM-5 zeolite. The bands of the H_3O^+ ion at 2885 and 2457 cm^{-1} are retained in the IR spectrum up to an equilibrium pressure of water of 10^{-1} Mbar,[9] *i.e.*, when no more than three H_2O molecules per H_3O^+ ion are present. Conversely, a dramatic decrease in the intensities of the bands of the $MeOH_2^+$ ion at 2900 and 2440 cm^{-1} is observed[11] when more than one MeOH molecule per $MeOH_2^+$ is present in the system (pressure 10^{-2} Mbar). Simultaneously, the δ(HOH) band for the methoxonium ion (1687 cm^{-1}) shifts to approximately 1620 cm^{-1}, and a new ν(OH) band appears at 3325 cm^{-1} indicating the formation of an H-bond between the $MeOH_2^+$ ion and a MeOH molecule. When up to three MeOH molecules per $MeOH_2^+$ ion are adsorbed (pressure 1 Mbar), the intensity of the ν(OH) band for the methanol cluster gradually increases, its frequency decreases to 3280 cm^{-1}, and the frequency of the δ(HOH) band for the $MeOH_2^+$ ion decreases further to 1580 cm^{-1}. Thus, an increase in the length of the cluster leads to strengthening of the H-bonds between the alcohol molecules within the cluster [decrease in ν(OH)] rather than to their weakening, as has been reported previously,[11] and, correspondingly, leads to the weakening of the H-bond of the methoxonium ion with the zeolite lattice [decrease in δ(HOH)].

The increase in the strength of the H-bonds as the number of units in the ...A—H...A—H...A—H... cluster increases is observed for all molecules linked by H-bonds. It is caused by a cooperative effect resulting in the enhancement of the proton-donating and proton-withdrawing abilities of the A—H groups (see, for example, Ref. 24).

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