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Spectra of Hydroxyl Groups in Zeolites in the Near-Infrared Region

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Diffuse reflectance ir spectra of hydroxyl groups in decationized and cationic forms of zeolites, X, Y, and mordenite have been studied for the first time in a wide spectral range, including the fundamental stretching vibrations of O–H bonds, their overtones and combination bands. Surface OH groups of amorphous aluminosilicate and silica gel have also been investigated. The combination bands of stretching and bending vibrations of OH groups are shown to be more sensitive to the environment of the hydroxyls than are the stretching vibrations (fundamental and overtones). The observation has been made that in the supercages of X-zeolite there are two different types of structural hydroxyls, which are not resolved in the fundamental region of the spectra, but differ both in their bending and combined frequencies. Cations introduced into zeolites by ion exchange influence the structural OH groups, resulting in a shift of their combination bands, in comparison with decationized samples, to lower or higher frequencies, depending on the nature of the cation and on the zeolite structure. The change in the bending frequencies of different OH groups is considered to be connected with the strength of their coordination to the neighboring aluminum atoms. The Morse function parameters of the potential curves x_e and ν_e and the isotopic effects of OH and OD groups in zeolites are calculated. The applicability of these data to characterize the acidic properties of OH groups is discussed.

INTRODUCTION

There are numerous papers on ir-spectroscopic studies of hydroxyl groups of zeolites of different composition (*1*, *2*). The spectra have been investigated, however, only in the region of the fundamental stretching vibrations of O–H bonds. At the same time, the ir spectra of surface hydroxyl groups are known to include some other absorption bands, belonging to bending vibrations, combination of several vibrations and overtones (*3–5*). Such studies allow a better characterization of structural and chemical properties of hydroxyl groups.

Measurements of ir spectra of hydroxyls in a wide spectral range encounter, however, some experimental difficulties. For instance, the bending vibrations of structural OH groups, with their frequencies in the range 700–1100 cm^{-1}, cannot be observed directly on the background of strong absorption bands of Al–O and Si–O vibrations of the zeolite and aluminosilicate framework. On the other hand, the combination bands and overtones, which are located in the near-ir region (above 4000 cm^{-1}), cannot be investigated using standard transmittance ir spectroscopy of the pellets because of low intensity of these bands and low transparency of the samples in this spectral range. On the contrary, the ability of zeolites to scatter the light in the near-ir region makes it possible to use for such study diffuse reflectance spectroscopy of powdered samples whose sensitivity, as will be shown below, is much higher than that of transmittance ir spectroscopy of the pellets. This technique has not been widely used so far since in the fundamental region the reflectance ir spectra have lower resolution than the transmittance spectra of the pellets (*6*).

The present work is the first attempt to investigate the ir spectra of hydroxyl groups of decationized and cationic forms of different zeolites in a wide spectral range (3300–11000 cm^{-1}), including combination bands and overtones, in addition to the fundamental stretching vibrations of O–H bonds. The spectra of hydroxyl groups of

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amorphous aluminosilicate and silica gel were also examined. In the discussion of the experimental results attention is mainly paid to the analysis of the combination and bending frequencies, which proved to be more sensitive to the nearest structural environment of hydroxyl groups than did the stretching vibrations. In addition, the shape of the potential curves of OH groups is analyzed and the isotopic effects, ρ, characterizing a change of the frequencies of the stretching vibrations of different hydroxyls due to substitution of a H atom by a D atom, are calculated.

EXPERIMENTAL

In our work decationized and cation-exchanged zeolites X, Y, and mordenite were used. The initial Na samples with a crystallinity of 90% were preliminarily calcined in air at 770 K for 8 h. NH_4 forms were obtained by ion exchange of the Na-zeolite with a 0.2 *M* aqueous solution of NH_4Cl.

Cation-exchanged samples were prepared by exchange with 0.05–0.1 *M* solutions of nitrates of Mg, Ca, Sr, Ba, La, and Ce(III) at a pH within the limits of 7.2–7.6 and 5.5–5.8 for the salts of alkaline-earth and rare-earth metals, respectively. The data on the chemical analysis of the zeolites are presented in Table 1.

After drying at 350 K in air the powdered samples (30–60 mesh) were placed in thin-walled quartz ampoules with a diameter of 5 mm and then were heated under vacuum for 8 h at 650 and 770 K for H-zeolites and cationic forms, respectively. The rate of the temperature increase was about 0.5 and 10 K/min for decationized and cation-exchanged samples.

Partially deuterated decationized zeolites were prepared by treatment of the hydrogen forms with D_2O vapor at 470 K and a D_2O pressure of 3.3×10^3 N/m^2 followed by evacuation of the samples at 650 K.

The amorphous aluminosilicate and silica gel were heated under vacuum at 870 K for 8 h.

TABLE 1

Chemical Analysis of Zeolites

Sample	SiO_2/Al_2O_3	Extent of ion exchange[a] (%)		
		H^+	Na^+	Me^{n+}
NaX	2.5	—	100.0	—
HNaX-50	2.5	49.8	50.2	—
HNaX-77	2.5	77.1	22.8	—
MgX	2.5	—	45.7	54.3
CaX	2.5	3.2	18.1	78.7
SrX	2.5	4.0	14.2	81.8
BaX	2.5	5.0	10.3	84.7
NaY	4.7	2.0	97.2	—
HNaY-57	4.7	57.0	43.0	—
HNaY-80	4.7	79.7	20.3	—
MgY	4.7	—	38.3	61.7
CaY	4.7	2.8	29.2	68.0
SrY	4.7	4.6	27.2	68.2
BaY	4.7	5.7	25.8	68.5
LaY	4.7	9.3	33.6	57.1
CeY	4.7	14.5	23.8	61.7
NaM (mordenite)	10.0	—	100.0	—
HNaM	10.0	50.2	49.8	—
MgM	10.0	—	39.0	61.0
CaM	10.0	—	27.6	72.4
SrM	10.0	—	17.5	82.5

[a] Me denotes the polyvalent exchanged cation.

Diffuse reflectance spectra of evacuated powdered samples in the range 3300–11000 cm^{-1} were measured at room temperature using a double-beam Beckman "Acta M-YII" spectrophotometer. An ampoule was placed in front of the spectrophotometer's entrance slit and illuminated by unfiltered light. The intensity of the diffuse reflected light, coming to the spectrophotometer detector, was ~5% of that of the reference beam. Therefore, during recording of the spectra the reference beam was attenuated by a diaphragm with a variable slitwidth.

RESULTS AND DISCUSSION

In Fig. 1 the reflectance ir spectrum of the powdered mixture of the decationized zeolite HNaX-50 with an aerosil (1 : 1), and the transmittance spectrum of a pressed pellet of the same composition, are shown. The thickness of the pellet was chosen so

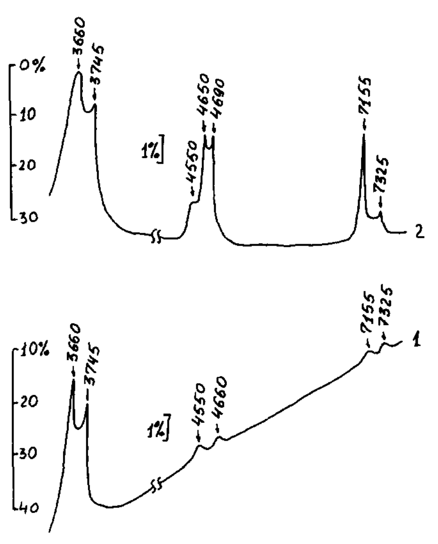


FIG. 1. Transmittance spectrum of the pellet (1) and diffuse reflectance spectrum (2) of the mixture (1 : 1) of the zeolite HNaX-50 with an aerosil.

that the intensities of the light passing through the pellet and that scattered by the powdered sample were equal. It is clearly seen that the intensities of the absorption bands of the spectra in Fig. 1 differ considerably. This is observed most distinctly in the region of the combination bands (4500–4800 cm^{-1}) and overtones of the hydroxyl groups (7000–7400 cm^{-1}). Indeed, in the transmittance spectrum of the pellet these lines are hardly observed whereas in the reflectance spectrum they are seen as strong absorption bands. Thus, reflectance spectroscopy considerably exceeds in sensitivity the standard technique of ir study of solids. This is likely to be due to an increase in the effective length of the optical path of the light in the powdered sample because of its repeated reflections and scattering by particles of the powder.

1. Decationized Zeolites

(a) Stretching vibrations and overtones. In Fig. 2 the reflectance spectra of decationized zeolites X, Y, and mordenite together with those of silica gel and amorphous aluminosilicate with a silica content of 80% are shown.

For all the samples the lines in the range 3300–3800 cm^{-1} are attributed to fundamental stretching vibrations of O–H bonds, i.e., they correspond to transition from the ground state to the first excited vibrational level (transition 0 → 1). Bands near 6800–7400 and 10,000–10,800 cm^{-1} belong to the first and second overtones of stretching vibrations of OH groups (transitions 0 → 2 and 0 → 3, respectively) (*7*).

To assign absorption bands in the fundamental and overtone regions, a comparison of the spectra of the samples with different degrees of ion exchange has been made. Thus, for zeolite HNaX-50 (Fig. 2) there is one main band at 3660 cm^{-1} in the fundamental region and a corresponding overtone line near 7155 cm^{-1}. When the extent of ion exchange increases from 50 to 80%,

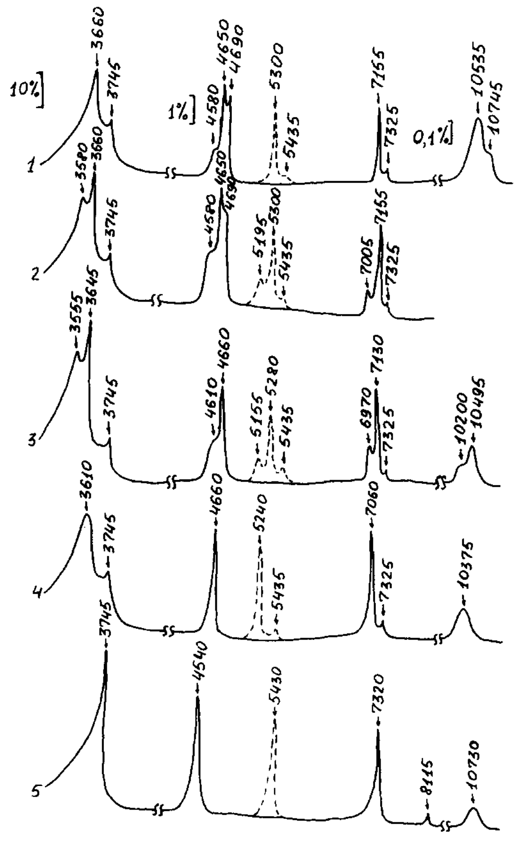


FIG. 2. Diffuse reflectance spectra of HNaX-50 (1), HNaX-77 (2), HNaY-80 (3), HNaM-50 (4) and silica gel (5).

bands at 3580 (in the fundamental) and 7005 cm^{-1} (in the overtone region) appear, which obviously belong to OH groups of the second type. Similar observations made for other zeolites indicate that to assign the band frequencies in the fundamental and overtone regions to certain types of OH groups the following two rules can be used:

(a) the higher the band intensity in the fundamental region, the higher the intensity of the overtone band;

(b) the lower the band frequency in the fundamental region, the lower the frequency of the overtone.

The frequencies of stretching vibrations and overtones for OH and OD groups of decationized zeolites and silica gel are listed in Table 2.

It has been shown recently (*7*), that a potential curve of OH groups of porous glasses may be approximated by a Morse function:

$$U(r) = D_e[1 - e^{-\alpha(r-r_e)}]^2. \qquad (1)$$

For this potential the frequencies of the transitions $0 \to n$ can be calculated using the equation

$$\nu_{0\to n}{}^{\mathrm{OH}} = n \cdot \nu_e{}^{\mathrm{OH}} - n(n+1)\nu_e{}^{\mathrm{OH}} x_e{}^{\mathrm{OH}}, \qquad (2)$$

where $\nu_e{}^{\mathrm{OH}}$ is the harmonic frequency of stretching vibrations, $x_e{}^{\mathrm{OH}} = \nu_e{}^{\mathrm{OH}}/4D_e$ is the parameter of anharmonicity, $D_e = D_0 + \frac{1}{2}\nu_e{}^{\mathrm{OH}}$, and D_0 is the dissociation energy of O–H bond.

The validity of this approximation was confirmed by linear plots of differences in the energies of the neighboring levels $n + 1$ and n versus the vibrational level number n. Similar straight lines were obtained for hydroxyl groups of the decationized zeolites. They are presented in Fig. 3 and prove the validity of the Morse function (1) approximation at least for the bottom of the potential curves of structural hydroxyls. This, in turn, enables us to determine the parameters of anharmonicity x_e and isotopic effects ρ, i.e., the ratio of the harmonic frequencies of the stretching vibrations of OH and OD groups. These values calculated from the equation (*8*)

$$\nu_{0\to n}{}^{\mathrm{OD}} = \frac{1}{\rho}\,\nu_e{}^{\mathrm{OH}} \cdot n - \frac{1}{\rho^2}\,\nu_e{}^{\mathrm{OH}}\, x_e{}^{\mathrm{OH}} \cdot n(n+1) \qquad (3)$$

are also presented in Table 2. It is seen that the values of ρ^2 are practically equal for different types of hydroxyl groups and coincide with the ratio of reduced masses for light and heavy hydroxyls ($\rho^2 = \mu_{\mathrm{OD}}/\mu_{\mathrm{OH}} = 1.889$). Therefore, the stretching vibration of the O–H bond is highly characteristic,

TABLE 2

Frequencies of Stretching Vibrations of OH Groups in Decationated Zeolites (cm^{-1})

Sample	$\nu_{0\to1}{}^{\mathrm{OH}}$	$\nu_{0\to2}{}^{\mathrm{OH}}$	$\nu_{0\to2}{}^{\mathrm{OD}}$	$\nu_{0\to3}{}^{\mathrm{OH}}$	$x_e \times 10^2$	ρ^2
(H,D)NaX-50	3660	7155	5300	10,535	2.18	1.890
	3745	7325	5435	10,745	2.10	1.885
(H,D)NaX-77	3580	7005	5195	—	2.05	1.885
	3660	7155	5300	—	2.18	1.890
	3745	7325	5435	—	2.10	1.885
(H,D)NaY-57	3555	6970	5155	10,200	1.95	1.890
	3645	7130	5280	10,495	2.07	1.887
	3745	7325	5435	—	2.10	1.885
(H,D)Na-mordenite	3610	7060	5240	10,375	2.15	1.887
	3745	7325	5435	—	2.10	1.885
SiO_2	3745	7320	5430	10,730	2.10	1.885

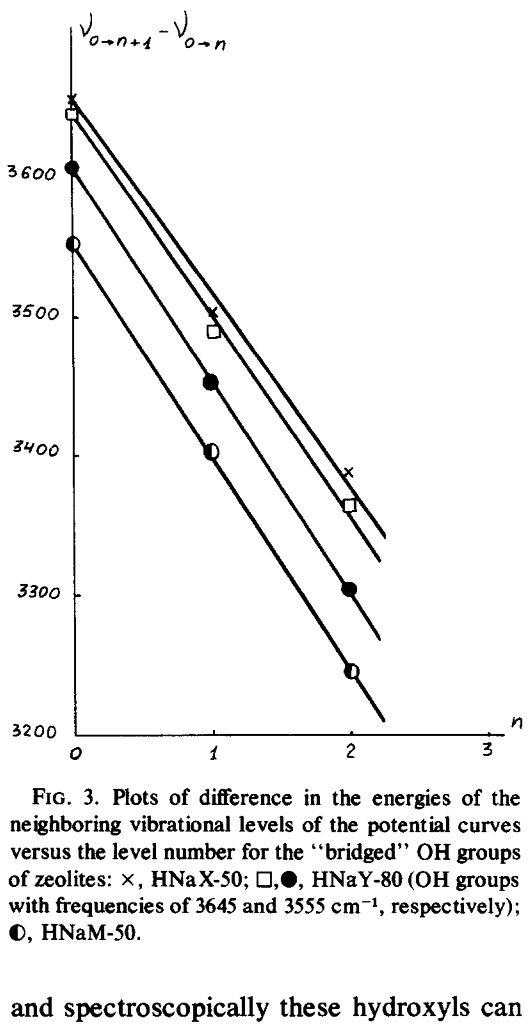


FIG. 3. Plots of difference in the energies of the neighboring vibrational levels of the potential curves versus the level number for the "bridged" OH groups of zeolites: ×, HNaX-50; □,●, HNaY-80 (OH groups with frequencies of 3645 and 3555 cm^{-1}, respectively); ◐, HNaM-50.

and spectroscopically these hydroxyls can be regarded as an isolated diatomic fragment O–H.

The parameters of anharmonicity for different types of OH groups in zeolites are also almost identical (2.1×10^{-2}) (see Table 2) and are close to the corresponding values for hydroxyl groups in other oxides (*7*). Therefore, for samples with high hydroxyl concentrations, having low resolution in the fundamental region of the diffuse reflectance spectra, the frequencies of the fundamental stretching vibrations can be calculated to a high degree of accuracy using band frequencies of the overtones. It is easy to show that for $x_e = 2.1 \times 10^{-2}$

$$\nu_{0\to1} = \nu_{0\to2}\left(\frac{1-2x_e}{2-6x_e}\right) \approx 0.4964\,\nu_{0\to2}. \quad (4)$$

Thus, Eq. (4) can be considered as a substantiation of the empirical rules mentioned above which have been applied for assignment of the bands in the fundamental and overtone regions of the spectra.

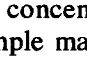
(*b*) *The combination bands of OH groups.* It was recently shown (*3, 4, 9*), that the absorption bands in the range 4500–4800 cm^{-1} correspond to a combination of fundamental stretching and bending vibrations ($\nu + \delta$) of surface hydroxyls.

It is also known (*8*), that generally the frequency of a combination band ($\nu_{\nu+\delta}$) is lower than the sum of the frequencies of fundamental stretching ($\nu_{0\to1}$) and bending ($\delta_{0\to1}$) vibrations. This difference is caused by interaction of these two vibrations. Let us estimate the magnitude of such interaction. As an example, we shall consider the spectrum of silica gel in the near-ir region (Fig. 2). The high concentration of Si–OH groups in this sample makes it possible to measure the second combination band frequency ($\nu_{2\nu+\delta}$). For silanol groups this value is equal to 8115 cm^{-1}.

An expression for the levels of vibrational energy of the triatomic fragment Si–O–H in the general form is

$$\begin{aligned} E(n_1,n_2,n_3) = {} & \nu_1(n_1+\tfrac{1}{2}) + \nu_2(n_2+\tfrac{1}{2}) \\ & + \nu_3(n_3+\tfrac{1}{2}) - X_{11}(n_1+\tfrac{1}{2})^2 \\ & - X_{22}(n_2+\tfrac{1}{2})^2 - X_{33}(n_3+\tfrac{1}{2})^2 \\ & - X_{13}(n_1+\tfrac{1}{2})(n_3+\tfrac{1}{2}) - X_{12}(n_1+\tfrac{1}{2}) \\ & \cdot(n_2+\tfrac{1}{2}) - X_{23}(n_2+\tfrac{1}{2})(n_3+\tfrac{1}{2}). \quad (5) \end{aligned}$$

Here the indexes 1, 2, and 3 belong to the stretching vibration of O–H group, the bending vibration of the angle



and the stretching vibration of the bond Si–O, respectively; n_i is the number of the vibrational level; ν_i is the harmonic frequency of the *i*th vibration; X_{ij} are the constants, characterizing either anharmonicity of the vibrations ($i = j$) or interaction of *i*th and *j*th vibrations ($i \neq j$).

The combination frequencies can be represented in the following form:

$$\nu_{\nu+\delta} = E(1,1,0) - E(0,0,0) = \nu_1 + \nu_2 - 2X_{11} - 2X_{22} - 2X_{12} - \tfrac{1}{2}X_{23} - \tfrac{1}{2}X_{13},$$

$$\nu_{2\nu+\delta} = E(2,1,0) - E(0,0,0) = 2\nu_1 + \nu_2 - 6X_{11} - 2X_{22} - \tfrac{7}{2}X_{12} - \tfrac{1}{2}X_{23} - X_{13} \quad (6)$$

or after a simple transformation:

$$\nu_{\nu+\delta} = (\nu_1 - 2X_{11} - \tfrac{1}{2}X_{12} - \tfrac{1}{2}X_{13}) + (\nu_2 - 2X_{22} - \tfrac{1}{2}X_{12} - \tfrac{1}{2}X_{23}) - X_{12}, \quad (7)$$

$$\nu_{2\nu+\delta} = (2\nu_1 - 6X_{11} - X_{12} - X_{13}) + (\nu_2 - 2X_{22} - \tfrac{1}{2}X_{12} - \tfrac{1}{2}X_{23}) - 2X_{12}. \quad (8)$$

It is easy to show using Eq. (5), that the terms, collected in the first parentheses in Eqs. (7) and (8), are equal to the frequencies of the fundamental stretching vibration and the first overtone, respectively, and that the terms gathered in the second parentheses to the bending frequency ($\delta_{0\to1}$).

Therefore,

$$\nu_{\nu+\delta}{}^{\mathrm{OH}} = \nu_{0\to1}{}^{\mathrm{OH}} + \delta_{0\to1}{}^{\mathrm{OH}} - X_{12},$$

$$\nu_{2\nu+\delta}{}^{\mathrm{OH}} = \nu_{0\to2}{}^{\mathrm{OH}} + \delta_{0\to1}{}^{\mathrm{OH}} - 2X_{12}. \quad (9)$$

Hence, the observed combination frequency is equal to the sum of the corresponding frequencies with an accuracy of that of the coefficient of their interaction (X_{12}). By solving Eqs. (9) we obtained for Si–OH groups of the silica gel,

$$\delta_{0\to1}{}^{\mathrm{OH}} = 795 \pm 5\ \mathrm{cm}^{-1},$$

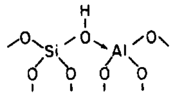
$$X_{12} = 0 \pm 5\ \mathrm{cm}^{-1}.$$

The corresponding value of the parameter X_{12} for the structural hydroxyls of X-zeolite is found to be very close to that calculated for Si–OH groups.

Therefore, one can deduce that the combination frequency to a high degree of accuracy represents the sum of frequencies $\nu_{0\to1}{}^{\mathrm{OH}}$ and $\delta_{0\to1}{}^{\mathrm{OH}}$. Thus, reflectance spectroscopy applied to the near-ir region makes it possible to investigate the bending vibrations of surface hydroxyls together with the stretching vibrations.

Let us now analyze the experimental data. We will characterize the different types of OH groups in zeolites by the frequency of the fundamental stretching vibrations as is accepted in the literature.

Absorption bands near the 3560 and 3650 cm^{-1} in the spectra of decationized zeolites X and Y, as well as the lines at 3610 cm^{-1} for H forms of mordenite, are attributed to structural hydroxyl groups of the "bridged" type (*2*):



(10)

The "bridged" hydroxyls of mordenite are assumed to have the strongest acidic properties among OH groups observed in different zeolites (*10*). In the spectrum of decationized mordenite there is only one absorption band in the fundamental, overtone, and combination regions (Fig. 2). In this case the assignment of the combination band at 4660 cm^{-1} is obvious: it corresponds to the "bridged" OH groups with the frequency of the stretching vibration of 3610 cm^{-1}, for which the frequency of the bending vibration is equal to 1050 cm^{-1} ($\delta = \nu_{\nu+\delta} - \nu_{0\to1}{}^{\mathrm{OH}}$).

The faujasites present a more complicated case, since they contain "bridged" OH groups with two frequencies of stretching vibrations near 3650 and 3560 cm^{-1}. The hydroxyls of H-faujasites, with absorption bands at 3650 and 3560 cm^{-1}, are commonly accepted (*11*) to be localized in the supercages and sodalite cages of zeolite framework, respectively, the latter being inaccessible to large molecules of adsorbate. This was used in assigning the combination bands in the spectra of faujasites, since the adsorption of 1,4-dioxane leads to the disappearance of the bands with $\nu_{0\to1} = 3650$ cm^{-1}, $\nu_{\nu+\delta} = 4650$–4695 cm^{-1}, the corresponding hydroxyls being located in the supercages of the zeolite framework (see Fig. 2).

The combination frequencies of "bridged" hydroxyl groups, having an absorption band at 3650 cm^{-1} in the fundamental region, are different for zeolites X and Y. In the spectrum of zeolite Y this type of OH group is characterized only by one combination band near 4660 cm^{-1}, whereas for zeolite X there are two combination bands with frequencies of 4655 and 4690 cm^{-1} (Fig. 2).

Analysis of the spectra of zeolite X in the region of the combination bands shows also that a variation in the degree of ion exchange of Na^+ by NH_4^+ affects the ratio of the band intensities. Thus, in zeolite X with a degree of ion exchange of 40–50% both types of hydroxyl groups, with a frequency of stretching vibrations of 3660 cm^{-1}, are present in comparable concentrations. At a higher extent of exchange (80%) the OH groups with a low frequency of combination band predominate, as in this case a high-frequency component is detected only as a shoulder.

Therefore, it can be concluded, that the band at 3660 cm^{-1} in the spectrum of zeolite X can be considered as the superposition of at least two bands, corresponding to two different types of OH groups. These hydroxyls localized in supercages differ only in their combination frequencies and are not resolved in the fundamental and overtone regions. This result is in agreement with the conclusion of Jacobs and Uytterhoeven (*12*), who resolved graphically the ir spectra of faujasites in the fundamental region of stretching vibrations of O–H bonds into several Gaussian components, corresponding to different types of OH groups.

The existence in zeolite X of two types of hydroxyls, which differ only in their bending frequencies, may reflect a real distribution of aluminum atoms in the framework, resulting in the difference of the "bridged" hydroxyls in their local structural environment, i.e., in the number of neighboring AlO_4 tetrahedra.

The bands near 3745 cm^{-1} are usually assigned to the "terminal" Si–OH groups of an impurity of an amorphous phase of silica, since a similar absorption band is observed in the spectra of silica gel. The nature of these OH groups is usually considered to be the same in silica gel, aluminosilicates, and zeolites (*11*). The different frequencies of their combination bands provide, however, evidence for their differences. Table 3 shows the frequencies of bending vibrations (δ) of different types of OH groups observed in zeolites, amorphous aluminosilicates, and silica gel. The values of δ were calculated by subtraction of the fundamental frequencies of the stretching vibrations from the corresponding combination frequencies. This parameter for the "terminal" Si–OH groups of silica ($\delta = 795$ cm^{-1}) is 30–40 cm^{-1} lower than that of Si–OH groups in faujasites and amorphous aluminosilicates. Therefore, the band at 3745 cm^{-1} in the spectra of zeolites X and Y should be ascribed rather to impurity of amorphous aluminosilicate than to the hydroxyls of amorphous silica.

Analysis of the data presented in Table 3 shows also that the frequencies of bending vibrations of "bridged" hydroxyl groups in zeolites are 180–250 cm^{-1} higher than that of terminal Si–OH groups. This may be due to the influence of the coordination of oxygen atom of the "bridged" OH group to the neighboring aluminum atom in the fragment (10) on the bending vibrations.

Moreover, the "bridged" OH groups of zeolites X, Y, and mordenite, which are known to have different acidity, also differ in the frequencies of their bending vibrations (see Table 3). Hence, it is reasonable to suggest that there is a qualitative relationship between the extent of polarization of the "bridged" hydroxyls and the strength of their coordination to neighboring aluminum atoms. The bending force constant and the bending frequency would increase with the strength of coordination. Simultaneously, the stretching force constant of the O–H bond would decrease because of polarization of the hydroxyl group (*13*). This is in agreement with the highest frequencies of the bending vibrations for "bridged" OH groups of mordenite ($\delta = 1050$ cm^{-1}), which is considered

TABLE 3

Combination and Bending Frequencies of Different OH Groups in Zeolites (cm^{-1})

Type of OH group	Sample	$\nu_{0\to1}^{OH}$	$\nu_{0\to1}^{OH} + \delta_{0\to1}^{OH}$	$\delta_{0\to1}^{OH}$
Terminal Si–OH	SiO_2	3745	4540	795
	SA-80[a]	3745	4565	820
	Mordenite	3745	4550	805
	Zeolite Y	3745	4570	825
	Zeolite X	3745	4580	835
"Bridged"$\equiv$Si(OH)Al$\equiv$	Decationated X (in supercages)	3660	4650 4690	990 1030
	Cationic X	3660	4620 4675	960 1015
	Decationated Y (in supercages)	3645	4660	1015
	Cationic Y	3645	4670	1025
	Decationated Y (in sodalite cages)	3555	4610	1055
	Decationated M	3610	4660	1050
	Cationic M	3620	4675	1055
MgOH	MeOH groups in cationic forms of faujasites	3595	4550	955
CaOH		3590	4530	940
SrOH		3600	4515	915
BaOH		3610	4495	890
LaOH		3520	4230	710
CeOH		3535	4230	695

[a] Amorphous aluminosilicate with silica content of 80%.

to have the strongest acidity, and with the lowest bending frequency of the weakly acidic OH groups in zeolite X ($\delta = 990$ cm^{-1}).

On the other hand, the high frequencies of bending vibrations of the hydroxyls located in the sodalite cages (the frequency of the stretching vibrations near 3560 cm^{-1}) can be explained by the formation of a hydrogen bond with an oxygen atom of the six-membered ring of zeolite.

Consequently, analysis of the combination frequencies allows one to distinguish the differences in the properties of the OH groups more clearly, which in some cases cannot be detected by standard ir spectroscopy in the fundamental region of stretching vibrations. In other words, the combination frequencies of hydroxyls are much more influenced by their neighboring environment than the frequencies of stretching vibrations, since the bending vibrations seem to be less characteristic than the stretching ones. That is why the combination frequencies provide deeper information on the structure and possibly on acidic properties of surface OH groups, than the frequencies of stretching vibrations which are highly characteristic.

2. *Cation-Exchanged Zeolites*

Figure 4 shows the reflectance spectra of zeolites CaX, CaY, CaM, NaX, and NaY. The positions of the bands belonging to the "bridged" OH groups of the corresponding decationized samples are marked in the spectra of Ca-zeolites by broken lines. Table 4 summarizes the band frequencies.

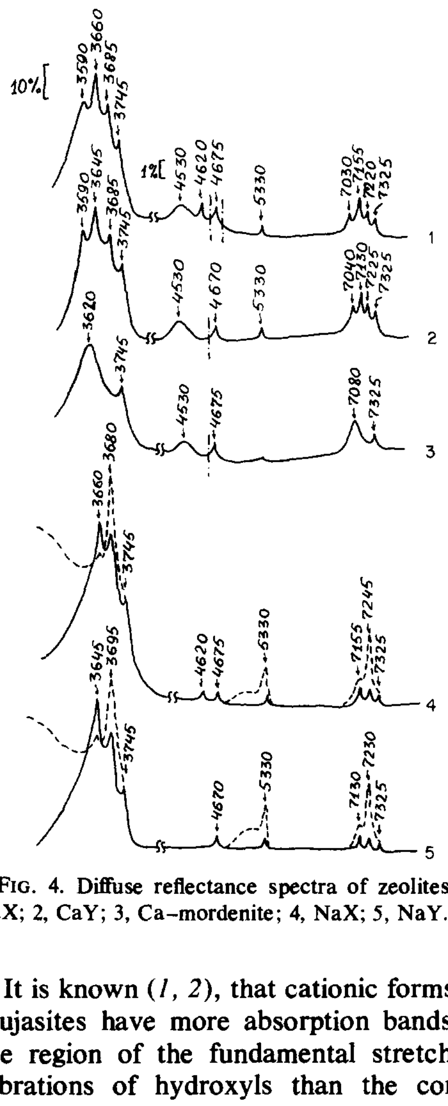


FIG. 4. Diffuse reflectance spectra of zeolites: 1, CaX; 2, CaY; 3, Ca-mordenite; 4, NaX; 5, NaY.

It is known (*1*, *2*), that cationic forms of faujasites have more absorption bands in the region of the fundamental stretching vibrations of hydroxyls than the corresponding hydrogen forms. First, additional bands are connected with the hydroxyls which are formed during hydrolysis of exchanged cations at high temperatures of sample treatment:

$$Me(H_2O)^{n+} \rightarrow Me(OH)^{(n-1)+} + H^+. \quad (11)$$

These Me-OH groups are characterized by absorption bands near 3520-3600 cm^{-1}, depending on the nature of the cation. Second, the bands at 3680-3690 cm^{-1} in the spectra of these zeolites are assigned to stretching vibrations of O-H bonds in water molecules coordinated with polyvalent cations (*14*). This assignment is confirmed by a comparison of the diffuse reflectance spectra of zeolites NaX and NaY heated at 770 K in air (broken lines in Fig. 4) and under vacuum (solid lines). The samples pretreated under vacuum differ from those calcined in air by a sharp decrease in the intensities of the bands at 3680 cm^{-1} in the fundamental region and of the line near 5330 cm^{-1}, which is characteristic of the combination band of water. At the same time, the bands in the range 4500-4800 cm^{-1} corresponding to the structural hydroxyl groups remain unaffected.

The spectrum of Ca-mordenite (Fig. 4) has only one broad line in the region of stretching vibrations with a maximum at 3620 cm^{-1}. This band can be assigned both to the "bridged" hydroxyls and to Ca-OH groups, since they have frequencies of stretching vibrations, which are close together. The selection between these possibilities is provided by the region of combination bands, where the "bridged" and Ca-OH groups are characterized by lines at 4680 and 4530 cm^{-1}, respectively. It can be seen also, that polyvalent cations influence the "bridged" OH groups, resulting in a shift of their combination bands by 10-15 cm^{-1} to higher frequencies as compared with the H form. Similar shifts of the combination bands (by 10-15 cm^{-1}) are also observed for the cation-exchanged Y-zeolites (Fig. 4, Table 4).

Analysis of the data presented in Tables 3 and 4 shows, that in the spectra of cation-exchanged zeolites X, as in the case of decationized forms, there are two combination bands corresponding to the one frequency of stretching vibration at 3660 cm^{-1}. This indicates that in the supercages of the cationic forms of X-zeolite there are also two different types of "bridged" OH groups, which can be distinguished only in this spectral range.

It should also be noted that for zeolite X, as for other cation-exchanged zeolites under study the combination frequencies and hence the bending frequencies of structural hydroxyls are somewhat different from those

TABLE 4

Band Frequencies in the Spectra of Cation-Exchanged Zeolites

Zeolite	$\nu_{0\to1}^{OH}$	$\nu_{0\to1}^{OH} + \delta$	$\nu_{0\to2}^{OH}$	Zeolite	$\nu_{0\to1}^{OH}$	$\nu_{0\to1}^{OH} + \delta$	$\nu_{0\to2}^{OH}$
NaX	3660	4620	7155	CaY	3595	4530	7040
		4680			3645	4670	7130
	3680	5330	7245		3685	5330	7225
	3745	—	7325		3745	—	7325
MgX	3595	4550	7085	SrY[a]	—	4545	—
	3660	4620	7155		3645	4670	7140
		4670			3685	5330	7220
	3695	5330	7235		3745	—	7325
	3745	—	7325				
CaX	3590	4530	7030	BaY[a]	—	4535	—
	3660	4615	7150		—	4670	—
		4675			3745	—	7325
	3685	5330	7220	MgM[a]	3620	4530	7080
	3745	—	7325			4670	
					3745	—	7325
SrX[a]	3600	4515	7040				
	3655	4625	7150	CaM[a]	3620	4530	7080
		4675				4675	
	3685	5330	7215		3745	—	7325
	3745	—	7325	SrM[a]	3620	4525	7080
BaX	3610	4495	7085			4670	
	3660	4625	7155		3745	—	7325
		4670					
	3685	5330	—	LaY	3520	4230	6910
	3745	—	7325		3645	4670	7125
					3685	5330	7220
NaY	3645	4670	7130		3745	4570	7325
	3695	5330	7230				
	3745	—	7325	CeY	3535	4230	6925
					3650	4670	7125
MgY	3600	4550	7070		3685	5330	7220
	3645	4670	7140		3745	4580	7325
	3690	5330	7230				
	3745	—	7325				

[a] Values of $\nu_{0\to1}^{OH}$ were calculated from the $\nu_{0\to2}^{OH}$ frequencies.

of the hydrogen forms. The reason for this difference is not clear. It may result from a change in the local electric charge in the zeolite framework caused by ion exchange or from direct interaction of structural hydroxyls with cations, which give rise to a change in the strength of the coordination of an oxygen atom of a OH group to a neighboring aluminum atom.

Analysis of the combination bands allows us also to calculate the frequencies of bending vibrations of Me–OH groups. They are listed in Table 4 and show a constant decrease with an increase of the cation mass in the following sequence:

$$\mathrm{MgOH} > \mathrm{CaOH} > \mathrm{SrOH} > \mathrm{BaOH} > \mathrm{LaOH} > \mathrm{CeOH}.$$

Thus, investigation of the combination frequencies in the ir spectra of hydroxyl groups of cation-exchanged zeolites permits us to resolve more clearly the bands of structural hydroxyls of different types, and to distinguish them from those of water or OH groups connected with polyvalent cations. This becomes possible because of differences in their bending frequencies which are 700–900 cm^{-1} for Me–OH groups, 990–1050 cm^{-1} for "bridged" hydroxyls, and about 1650 cm^{-1} for water molecules.

CONCLUSION

The results obtained in this paper demonstrate some new possibilities of diffuse reflectance ir spectroscopy in studying hydroxyl groups in zeolites. They show that the analysis of the combination bands can provide better information on the real distribution of OH groups, and on their structural environment, than do their stretching frequencies. It is also possible that the combination frequencies contain more profound information on the nature of the acidic properties of hydroxyl groups.

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