

## INTERACTION OF WATER WITH CoNaX ZEOLITES

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Interaction of water with NaX zeolites and CoNaX zeolites of various  $\text{Co}^{2+}$  content, dehydrated at  $400^\circ\text{C}$ , was investigated by means of electronic and infrared spectroscopy. In the case of CoNaX zeolites both water adsorbed on  $\text{Na}^+$  ions and water related to the presence of  $\text{Co}^{2+}$  ions was found. In the latter case water in the molecular form was characteristic for small adsorbed amounts which disappeared upon further adsorption, while hydroxyls on  $\text{Co}^{2+}$  ions and on the zeolite skeleton were being formed. These processes were accompanied by distortions of the original  $T_d$  cobalt complex. During further adsorption, mutual influencing of the adsorbed water molecules and interaction with OH groups took place; the symmetry of the  $\text{Co}^{2+}$  ligand field practically did not change in this region. Only in the region of high water content the  $T_d$  symmetry of the  $\text{Co}^{2+}$  complex changed to  $O_h$ . The  $\text{Co}^{2+}$  ion content as well as the content of adsorbed water significantly influenced the skeletal vibrations of the zeolite. These vibrations indicated changes in the lattice parameters connected both with the changes in the  $\text{Co}^{2+}$  location, and with the formation of hydroxyl groups and the presence of water. It followed from the changes in skeletal vibrations, largest in the region of water dissociation, that this process was connected with the migration of  $\text{Co}^{2+}$  in the zeolite lattice.

It follows from published data<sup>1</sup> that a change in the water content in cation zeolite forms is accompanied by a series of processes which depend both on the zeolite composition and on whether hydration or dehydration occurs. In this paper we devoted our attention to the X-form zeolites containing  $\text{Co}^{2+}$  ions, in view of their catalytic activity in oxidation reactions<sup>2</sup>. One of the reaction components in these reactions is water whose presence may considerably influence the properties of both the Si—Al skeleton and metal cations. It is known that  $\text{Co}^{2+}$  ions in these zeolites form hexaquo complexes, while the zeolites dehydrated at  $400^\circ\text{C}$  exhibit tetrahedral coordination<sup>3-7</sup>. During the dehydration first water is desorbed<sup>8</sup> and then dehydroxylation occurs on the expenses of the hydroxyl groups bound partly to the  $\text{Co}^{2+}$  and partly to the Al—Si—O skeleton<sup>9</sup>.

Because enough attention has been paid to the dehydration, we concentrated onto the investigation of the interaction of water with samples previously dehydrated at  $400^\circ\text{C}$ . The aim of this study has been to obtain more detailed information on adsorption centers of the zeolites, on conditions of water dissociation, and on changes of the  $\text{Co}^{2+}$  coordination; at the same time, attention has been paid to skeletal vibrations of the zeolites. Therefore, infrared spectroscopy and electronic diffusion reflectance spectroscopy was employed in this study.

## EXPERIMENTAL

*Chemicals.* The composition of the studied zeolites is given in Table I. The cobalt forms of the zeolites were prepared by exchanging  $\text{Na}^+$  ions of NaX zeolite in a  $\text{CoCl}_2$  solution at  $50^\circ\text{C}$  at such conditions that no hydrolysis took place. For infrared spectra measurements, the zeolites were formed into plates  $3 \times 1 \text{ cm}^2$ , of 10–50 mg weight, by  $700 \text{ kg/cm}^3$  pressure. For reflection spectra measurements, zeolites in the powder form were used; sample weight was about 1 g. In both cases the samples were dehydrated in a standard way in vacuum cells of the spectrometers at  $400^\circ\text{C}$  for 16 hours at the pressure of  $1.3 \cdot 10^{-4} \text{ Pa}$ . Water was purified by multiple freezing and evacuation, carbon dioxide was removed by barium hydroxide addition.

*Apparatus and measurements.* Infrared spectra were measured over the region  $4000\text{--}350 \text{ cm}^{-1}$  by means of a Perkin-Elmer 621 spectrometer using a screen in the reference beam. The vacuum cell was described elsewhere<sup>10</sup>. The adsorption was studied at the infrared beam temperature, the cell compartment of the spectrometer was kept at  $40^\circ\text{C}$ . The registration of the spectrum was started 30 min after the particular water dose admission (registration time 90–120 minutes); repeated recording did not show any substantial changes in the spectrum. In comparing band heights of the particular samples in some cases the value  $A_v = d^{-1} \log(I_0/I)$  was used; here,  $d$  is the sample thickness in  $\text{mg/cm}^2$ ;  $I$  and  $I_0$  are the transmittance of the sample and the corresponding base line at the wavenumber  $\nu$ , respectively. Electronic spectra over the range  $25000\text{--}14000 \text{ cm}^{-1}$  were measured by the reflection techniques using an Optica Milano CF4 NI instrument with the  $R_{0,D}$  geometry. The spectra were evaluated with the use of the Kubelka–Munk function  $f(R_\infty) = (1 - R_\infty)^2/2R_\infty = k/s$ , where  $k$  and  $s$  are the absorption and the scattering coefficient, respectively,  $R_\infty$  is the reflectance of an infinite sample layer (simulated by a 2–3 mm layer)<sup>4</sup>, related to the reflectance of an ideal white standard ( $R = 1$ ). The standard was dehydrated MgO in an evacuated cell.

TABLE I  
Composition of Zeolites

Zeolite	Chemical composition	Weight loss <sup>a</sup> (%)	Cubo/g . $10^{-20b}$	$\text{Na}^+$ : cubo	$\text{Co}^{2+}$ : cubo
NaX	$(\text{Na}_2\text{O})_{0.95}(\text{CaO})_{0.03}$ $\text{Al}_2\text{O}_3(\text{SiO}_2)_{2.66}$	25.0	2.73	9.8	—
CoNaX-21	$(\text{Na}_2\text{O})_{0.86}(\text{CoO})_{0.21}(\text{CaO})_{0.01}$ $\text{Al}_2\text{O}_3(\text{SiO}_2)_{2.76}$	25.3	2.67	8.8	1.1
CoNaX-47	$(\text{Na}_2\text{O})_{0.50}(\text{CoO})_{0.47}(\text{CaO})_{0.02}$ $\text{Al}_2\text{O}_3(\text{SiO}_2)_{2.55}$	27.2	2.61	5.2	2.4

<sup>a</sup> Dehydration at  $400^\circ\text{C}$ , 16 hours,  $1.3 \cdot 10^{-4} \text{ Pa}$ ; <sup>b</sup> Number of cubooctahedrons (= 1/8 unit cell) per 1 g of hydrated zeolite.

## RESULTS

Infrared spectra of water adsorbed on NaX zeolite in dependence on the adsorbed amount were described in detail by Kiselev and coworkers<sup>11</sup>, in the region of both stretching and bending vibrations. In order to check the experimental arrangement, the spectra were measured by us, too; for a comparison with spectra of water adsorbed on CoNaX zeolites, they are given in Fig. 1a. It follows from these spectra that with the increasing adsorption intensities of the bands 3690, 3400, 3340, and 3230  $\text{cm}^{-1}$  increase; many authors dealt with their interpretation<sup>1</sup> and the bands

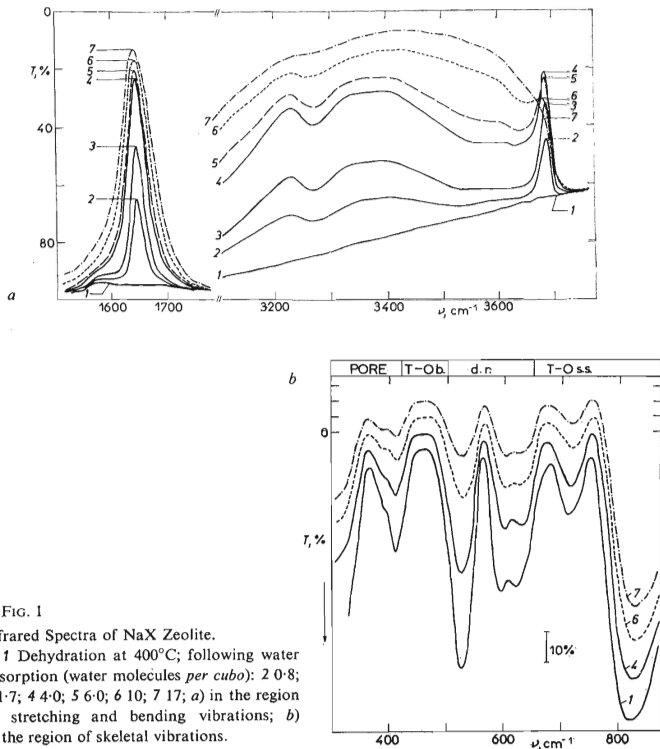


FIG. 1

## Infrared Spectra of NaX Zeolite.

1 Dehydration at 400°C; following water adsorption (water molecules *per cubo*): 2 0.8; 3 1.7; 4 4.0; 5 6.0; 6 10; 7 17; a) in the region of stretching and bending vibrations; b) in the region of skeletal vibrations.

are assigned to water adsorbed *via* oxygen to  $\text{Na}^+$  ions. From the water content of 6 water molecules *per cubo* up the band  $3690\text{ cm}^{-1}$  begins to decrease and eventually it disappears, while at the lower wavenumbers the absorption increases as early as at about  $3600\text{ cm}^{-1}$ ; the observed bands are broad and they overlap each other. This indicates that water molecules in the zeolite begin to influence each other. The band of bending vibrations of water adsorbed on NaX lies at  $1645\text{ cm}^{-1}$  and during the hydration it shifts to  $1640\text{ cm}^{-1}$ .

Changes in the NaX spectra in the region of skeletal vibrations during water adsorption are shown in Fig. 1b; the assignment of the bands according to Flanigen and coworkers<sup>12</sup> is given, too. These authors distinguish two classes of the zeolite skeletal vibrations: internal vibrations of lattice  $\text{TO}_4$  tetrahedrons ( $T = \text{Si}, \text{Al}$ ) and vibrations related to external links between the tetrahedrons, sensitive to lattice structure and to the presence of larger build-up units as double rings (hexagonal prisms) and large windows of zeolite cavities (twelve-membered windows). Thus, bands in the region  $1250\text{--}950\text{ cm}^{-1}$  are assigned to the asymmetric stretching mode  $\text{O—T—O}$ , in the region  $820\text{--}650\text{ cm}^{-1}$  to the symmetric stretching mode  $\text{O—T—O}$ , in the region  $500\text{--}420\text{ cm}^{-1}$  to the bending mode  $\text{T—O}$ . Bands in the region  $650$  to  $500\text{ cm}^{-1}$  are related to the presence of double rings (D6R) in the zeolite lattice, and bands at  $420\text{--}300\text{ cm}^{-1}$  are assigned to the breathing movement of the rings which form the windows of zeolite cavities, further on referred to as pore opening (PO). Bands in the region  $1250\text{--}950\text{ cm}^{-1}$  were so strong that we could not follow their changes and thus we confined our attention to the region  $900\text{--}350\text{ cm}^{-1}$ . It was found that due to the adsorption of water on NaX the over-all transmittance of the sample decreased and the minima were less clear, but the position of the bands did not change appreciably (Table II).

The adsorption of water on CoNaX-47 in the region  $4000\text{--}1200\text{ cm}^{-1}$  was accompanied by the appearance of bands whose position was the same as in NaX and, in addition, by new bands reflecting the presence of  $\text{Co}^{2+}$  ions in the zeolite (Fig. 2a). The height of the bands of the first group changed upon water adsorption in a similar way as with NaX, however, the  $3690\text{ cm}^{-1}$  band was with CoNaX-47 always substantially weaker at the same adsorbed amount. The bands of the second group showed — up to the water amount of 2.5 water molecules *per cubo* — an increase of the  $3575\text{--}80\text{ cm}^{-1}$  band, a decrease of the transmittance beginning at about  $3550\text{ cm}^{-1}$  and continuing towards lower wavenumbers, and a simultaneous increase of a new band at  $1660\text{ cm}^{-1}$ . Only further dose of water caused a marked increase of the  $3650\text{ cm}^{-1}$  band and the appearance of a maximum at  $3595\text{ cm}^{-1}$ . At the same time, in the region of bending vibrations of water, the band  $1640\text{ cm}^{-1}$  (formed also in NaX) began to play a dominant role, the  $1660\text{ cm}^{-1}$  band occurred as its shoulder only. Eventually, only the band  $1640\text{ cm}^{-1}$  was visible in the spectrum. From the water content of 6 water molecules *per cubo* up, the band  $3650\text{ cm}^{-1}$  started to lose its prominent character. According to the published data<sup>1,8,9</sup> some of the new bands

hang together with vibrations of OH groups formed in the dissociation of water: the bands  $3650, 3575-80\text{ cm}^{-1}$  with the vibrations of hydroxyls containing skeletal oxygen (lattice hydroxyls), the band  $3595\text{ cm}^{-1}$  with the vibrations of hydroxyls bound to cobalt. In the spectrum of skeletal vibrations of CoNaX-47 considerable changes were observed upon water adsorption (see Fig. 2b, and Table II for the band positions). The effect of  $\text{D}_2\text{O}$  adsorption on the skeletal vibration spectrum was essentially the same as that one of  $\text{H}_2\text{O}$ .

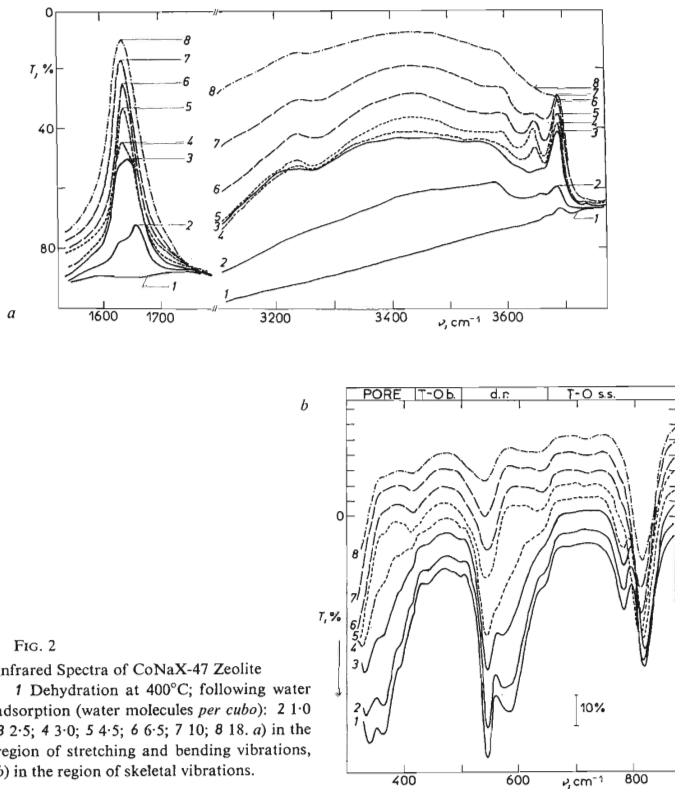


FIG. 2

#### Infrared Spectra of CoNaX-47 Zeolite

1 Dehydration at  $400^\circ\text{C}$ ; following water adsorption (water molecules per cubo): 2 1.0; 3 2.5; 4 3.0; 5 4.5; 6 6.5; 7 10; 8 18. a) in the region of stretching and bending vibrations, b) in the region of skeletal vibrations.

Spectra of the CoNaX-21 zeolite had after the water adsorption over all investigated wavenumber ranges the same character as the spectra of CoNaX-47. Only the bands which were the same as in NaX were more intense, while those connected with the presence of  $\text{Co}^{2+}$  had a lower intensity. As an illustration, Fig. 3a compares the spectra of all the three original samples (*i.e.* after the dehydration at  $400^\circ\text{C}$ ) over the range of skeletal vibrations. Marked differences between these spectra, observed in this case, did not show up with fully hydrated samples (Fig. 3b) due to the screening effect of water.

The electronic spectrum of the CoNaX-47 zeolite dehydrated at  $400^\circ\text{C}$  showed main absorption bands about  $8000$  and  $17000\text{ cm}^{-1}$ , corresponding to the tetrahedral symmetry of the  $\text{Co}^{2+}$  ligand field (Fig. 4). The  $17170\text{ cm}^{-1}$  band was assigned to the transition  ${}^4A_2 \rightarrow {}^4T_1(P)$ , its splitting at  $15300$  and  $18700\text{ cm}^{-1}$  to the spin-orbit interaction<sup>13</sup> or to the dynamic Jahn-Teller effect<sup>14</sup>. The second observed band

TABLE II

Positions of Maxima ( $\text{cm}^{-1}$ ) in Infrared Spectra of Zeolites Over the Wavenumber Range  $900\text{--}350\text{ cm}^{-1}$

NaX <sup>a</sup>		CoNaX-47		CaNaX-66 (ref. <sup>16</sup> )	CaY (ref. <sup>11</sup> )		Assignment <sup>12</sup>	
D $400^\circ\text{C}$	H 17 $\text{H}_2\text{O}$ ; ; cubo	D $400^\circ\text{C}$	H 18 $\text{H}_2\text{O}$ ; ; cubo	FH	D $470^\circ\text{C}$	D $400^\circ\text{C}$		H
		795			790			
760	760	750 715	755	775		710—750		T—O sym. stretch
690	690		690	700				
665	675	680 635			675		635	
615	615		615					
570	570	560 505	585 <sup>†b</sup>	580	580 <sup>↓</sup> 500	570	570 <sup>↑</sup>	double ring —
465	465	475 430	475	470	470 425	— 415	—	T—O bend —
400	400	390	395 <sup>↑</sup>	—	—	400 390	390 <sup>↑</sup>	pore opening
370	370	360	365 sh	—	—			

<sup>a</sup> D dehydrated, H after the following water adsorption in molecules per cubooctahedron, FH initial, fully hydrated, <sup>b</sup> <sup>†</sup>band intensity increases, <sup>↓</sup>band intensity decreases

at  $8200\text{ cm}^{-1}$  corresponded to the transition  ${}^4A_2 \rightarrow {}^4T_1(F)$  and exhibited a splitting ( $6600\text{ cm}^{-1}$ ). However, because of a rather bad resolution in this region the spectrum did not provide significant information comparable to that one from the region about  $17000\text{ cm}^{-1}$ . Therefore, during the water adsorption only the interval in the vicinity of  $17000\text{ cm}^{-1}$  was investigated. CoNaX-21 dehydrated at  $400^\circ\text{C}$  for 16 hours yielded the same spectrum, only its intensity was lower<sup>4</sup>.

During the interaction of the first water doses with the dehydrated CoNaX-47 zeolite (up to about 6 water molecules *per cubo*) a significant change in the position and in the splitting of the  $17170\text{ cm}^{-1}$  band took place; the change was towards a smaller splitting and the relative intensities of the particular bands were unaffected even if the intensity of the entire spectrum increased somewhat (less than 10%, see Fig. 4 and 5). During further hydration (about 6–13 water molecules *per cubo*) the band splitting did not change significantly. If the water content increased above 13 water molecules *per cubo*, the spectrum gradually changed to that one corresponding to the octahedral coordination of  $\text{Co}^{2+}$  in the hexaquo complex<sup>4</sup> (Fig. 4). The fol-

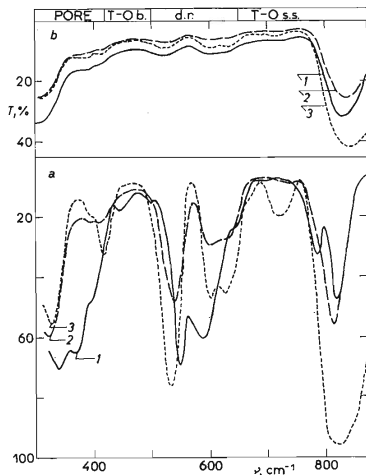


FIG. 3

Infrared Spectra of Zeolites

1 CoNaX-47, 2 CoNaX-21, 3 NaX; a) dehydration at  $400^\circ\text{C}$ , b) fully hydrated samples.

lowing transitions corresponded to this complex:  $8200\text{ cm}^{-1} \text{ } ^4T_{1g} \rightarrow \text{ } ^4T_{2g}$ ;  $15300\text{ cm}^{-1} \text{ } ^4T_{1g} \rightarrow \text{ } ^4A_{2g}$ ;  $19000\text{ cm}^{-1} \text{ } ^4T_{1g}(P) \rightarrow \text{ } ^4T_{1g}(F)$  with the splitting  $21500\text{ cm}^{-1}$  due presumably to the spin-orbit interaction.

## DISCUSSION

During the sorption over zeolites a non-homogeneous filling of zeolite cavities may take place – depending on the sorbate used and on its bond-strength with adsorption centers –, *i.e.* a preferential occupation of the cavities close to the surface. When measuring reflection spectra we observed that (in the case of the CoNaX + H<sub>2</sub>O system) a small water addition (about two water molecules *per cubo*) to CoNaX-47 dehydrated at 400°C in the reflection-spectra cell lead to a change of the colour from blue ( $T_d$  symmetry of Co<sup>2+</sup>) to pink ( $O_h$  symmetry) only in the surface layer in the cell throat. Thus the first zeolite levels were fully hydrated, while the zeolite in the lower layer at the cell window did not change (as confirmed by the spectrum).

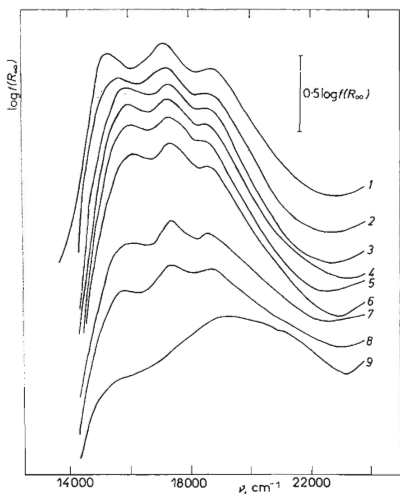


FIG. 4

### Reflection Diffusion Spectra of CoNaX-47 Zeolite

1 Dehydration at 400°C; following water adsorption (water molecules *per cubo*): 2 2.4; 3 5.0; 4 7.5; 5 10; 6 13; 7 17; 8 22; 9 26.



To remove this unpleasant phenomenon, the zeolite samples were mechanically stirred in vacuum apparatus before the reflection spectra were measured. The sample was then represented by the spectrum (Fig. 4) which was not a superposition of a spectrum of the fully dehydrated and fully hydrated zeolite. This confirmed the homogeneous distribution of water throughout the entire sample.

In the measurement of the infrared spectra, the zeolites in the form of plates  $3-5 \text{ mg/cm}^2$  (i.e.  $15-25 \mu\text{m}$ ) thick were used. After the interaction of water with thicker samples the character of changes in the spectra was the same. However, a prominent increase of the  $3650 \text{ cm}^{-1}$  band in the CoNaX-47 plate of  $5 \text{ mg/cm}^2$  showed up after the adsorption of three water molecules *per cubo*, while with the sample of  $16 \text{ mg/cm}^2$  the same effect took place as early as after the addition of 1.7 water molecules *per cubo*. The reason of this difference may be the non-homogeneous occupation of cavities. As far as other factors are concerned, e.g., adsorption of water on apparatus walls could play a role; however, an estimation showed that this effect was relatively small. We tried to minimize the influence of the inhomogeneous occupation of cavities by using samples as thin as possible. In comparing the results of infrared and electronic spectroscopy, we confined our attention to three main regions of characteristic changes in the zeolites in dependence on the water content: 0-6, 6-13, 13 and more water molecules *per cubo*.

#### Dehydrated Forms of Zeolites

Electronic spectra of CoNaX dehydrated at  $400^\circ\text{C}$  showed the tetrahedral symmetry of the oxygen ligand field of  $\text{Co}^{2+}$ . The observed large splitting of the  $17170 \text{ cm}^{-1}$  band ( $15300$  and  $18700 \text{ cm}^{-1}$ ) can be presumably ascribed to the dynamic pseudo-Jahn-Teller effect<sup>15</sup> which originates in the distorted tetrahedral complex of  $\text{Co}^{2+}$ .

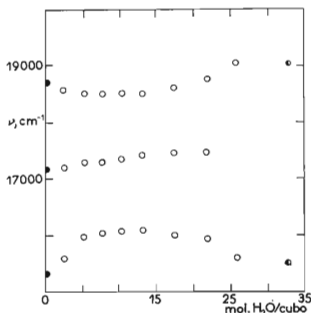


FIG. 5  
Dependence of the Band Position in the Reflection Diffusion Spectrum of CoNaX-47 Zeolite on the Adsorbed Water Amount (molecules *per cubo*)

● Dehydration at  $400^\circ\text{C}$ ; ○ partial hydration; ◐ full hydration.

In this complex three oxygen ligands come from skeletal zeolite oxygens, the fourth ligand may be a water molecule, a hydroxyl group, or an oxygen atom. The location of  $\text{Co}^{2+}$  ions in  $S_{I'}$ ,  $S_{II'}$ , or  $S_{II}$  sites corresponds to this arrangement. It followed from  $\text{D}_2 + \text{OH}$  exchange experiments<sup>8</sup> that one  $\text{Co}^{2+}$  ion falls on about one zeolite hydrogen. Therefore, one may conclude from purely electrostatic considerations and from the fact that no aluminium Lewis sites<sup>9</sup> were found that the fourth ligand is prevalingly an oxygen atom shared by two  $\text{Co}^{2+}$  ions:  $\text{O}_3(\text{latt})-\text{Co}-\text{O}-\text{Co}-\text{O}_3(\text{latt})$ . The location of these  $T_d$  complexes of  $\text{Co}^{2+}$  is most favourable geometrically inside of a sodalite unit in  $S_{I'}$  or  $S_{II'}$  sites. It follows from the electronic spectra (despite a lower intensity of spectra of  $O_h$  complexes in comparison with those of  $T_d$  complexes) that the zeolites dehydrated at  $400^\circ\text{C}$  probably do not contain  $\text{Co}^{2+}$  in  $S_I$  positions, *i.e.* in the  $O_h$  symmetry of the oxygen ligand field in hexagonal prisms. A consequence of the exchange of  $\text{Na}^+$  for  $\text{Co}^{2+}$  are changes in the lattice parameters and in the force field of the zeolites. These changes manifest themselves in the dependence of intensities and positions of bands of skeletal vibrations on the  $\text{Co}^{2+}$  ion content in the dehydrated zeolites. They concern both D6R and PO vibrations and stretching vibrations of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons (Fig. 3a, Table II). It remains an open question, how the vibrations of  $\text{CoO}_4$  tetrahedrons manifest themselves in the infrared spectra.

#### Water Adsorption

The results concerning the interaction of water with NaX are in agreement with those of Kiselev and coworkers<sup>11</sup>. The occurrence of the same bands of adsorbed water in the spectra of  $\text{CoNaX}$  and the dependence of the intensities of these bands on the  $\text{Na}^+$  ion content shows that sodium ions serve as adsorption centers even in the case of  $\text{CoNaX}$ . Water interacts with sodium *via* its oxygen atom and one of its OH bonds is strongly influenced by the interaction between the H atom and the skeletal oxygen of the zeolite. The number of water molecules adsorbed on  $\text{Na}^+$  ions of  $\text{CoNaX}$  increases with the total amount of water added.

The influence of  $\text{Co}^{2+}$  on the interaction of water with  $\text{CoNaX}$  dehydrated at  $400^\circ\text{C}$  manifests itself most prominently up to the total water content of 6 water molecules *per cubo*. After the initial water doses new form of adsorbed water was found due to the  $\text{Co}^{2+}$  presence. In this adsorbed water molecule (further on  $\text{H}_2\text{O}(\text{Co})$ ) both OH bonds are weakened to a similar extent, and its presence is indicated by the  $1660\text{ cm}^{-1}$  band and by an increased absorption in the region from  $3550\text{ cm}^{-1}$  towards lower wavenumbers. It is probable that  $\text{H}_2\text{O}(\text{Co})$  coacts in perturbing the force field of  $\text{CoNaX}$  which leads to the dissociation of water and to the formation of lattice hydroxyls within large cavities ( $3650\text{ cm}^{-1}$ ) and OH groups bound to  $\text{Co}^{2+}$  ions ( $3595\text{ cm}^{-1}$ ). A sudden increase of the bands assigned to these hydroxyls was found only after addition of a larger amount of water (from 3 water molecules *per cubo* up);

at the same time,  $\text{H}_2\text{O}(\text{Co})$  gradually ceased to appear in the spectrum. Also,  $\text{H}_2\text{O}(\text{Co})$  was not found after water adsorption on gently dehydrated zeolites in which hydroxyl groups were mostly preserved. Up to the water content of 6 water molecules *per cubo* the electronic spectra showed pronounced changes in the  $\text{Co}^{2+}$  ion ligand field, too. These changes can be explained by distortions of the original tetrahedron not only because of the  $\text{O}-\text{OH}-\text{H}_2\text{O}$  ligand exchange, but also by changes in the location of  $\text{Co}^{2+}$  ions in the zeolite lattice.

In the adsorption range 6–13 water molecules *per cubo*,  $\text{Co}^{2+}$  ions preserve the tetrahedral symmetry of the ligand field; their electronic spectra practically do not change. At these concentrations water molecules in the zeolite start to interact with each other, water presumably influences hydroxyl groups, too. Only at adsorbed amounts larger than 13 water molecules *per cubo*, substantial changes in the symmetry of the  $\text{Co}^{2+}$  ligand field take place, namely from the tetrahedral to octahedral symmetry. However, we cannot make any conclusions concerning the exact structure of the complexes in this region; the analysis of the infrared spectra was of no use either.

The infrared spectrum in the region of skeletal vibrations of the zeolites depends both on the  $\text{Co}^{2+}$  ion content and on the water content: in contrast with the CoNaX spectrum, the spectrum of NaX changed upon water adsorption only little (Fig. 1b, 2b). In the literature there has been so far only little information concerning the influence of water adsorption on skeletal vibrations of zeolites containing divalent cations. Flanigen and coworkers<sup>12</sup> compared spectra of CaY dehydrated at 200°C, 400°C, and rehydrated. Dyrkheev and coworkers<sup>16</sup> studied gradual dehydration of CaNaX-66 (Table II); the same type of changes was observed by us on the dehydrated CaNaX-60 during water adsorption. Changes in the spectra of skeletal vibrations were correlated<sup>12,16</sup> with lattice distortions and changes of the hexagonal prism symmetry caused by  $\text{Ca}^{2+}$  migration into or from  $S_1$  sites. During the dehydration of CoNaX-40 Dyakonov and coworkers<sup>17</sup> found — besides others — a decrease of the  $560\text{ cm}^{-1}$  band intensity (D6R vibrations); they explained this phenomenon by the  $\text{Co}^{2+}$  migration from  $S_1$  sites; this process was observed as early as at 200°C. However, it follows from our results: 1) in the zeolites dehydrated at 400°C  $\text{Co}^{2+}$  ions are located practically only in  $T_d$  complexes; in view of a lower intensity of the absorption bands of  $O_h$  complexes in their electronic spectra, these bands may not be fully resolved in the vicinity of the strong bands of the  $T_d$  complexes; however, the  $\text{Co}^{2+}$  migration from  $S_1(O_h)$  to  $S_1$ ,  $S_{II}$ , or  $S_{III}(T_d)$  sites upon water adsorption should necessarily lead to an observable substantial increase of the  $T_d$  band intensity; this effect was not observed experimentally; 2) in the samples dehydrated at 400°C the  $560\text{ cm}^{-1}$  band in the infrared spectra decreased markedly with the  $\text{Co}^{2+}$  content and a new band at  $635\text{ cm}^{-1}$  appeared; this indicates that the D6R vibrations are sensitive to the changes in the force field and in the lattice parameters caused by the localization of divalent cations in the sites neighbouring on hexagonal prisms

( $S_{I'}$ ,  $S_{II'}$ ,  $S_{II}$ ), not only inside the hexagonal prisms ( $S_I$ ); 3) during the water adsorption largest changes in intensities and positions of the bands D6R, PO, and also of stretching and bending vibrations of  $TO_4$  accompanied the water dissociation; at the same time, the ligand field of  $T_d$  complexes of  $Co^{2+}$  changes; the changes in the skeletal vibrations can be explained by the  $Co^{2+}$  migration from sodalites ( $S_{I'}$ ,  $S_{II'}$ ) to large cavities ( $S_{II}$ ); furthermore, the skeletal vibrations may be partially influenced by the formation of skeletal hydroxyls.

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