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# Investigation of the non-isothermal water desorption on alkali-metal cation-exchanged X-type zeolites: a temperature-programmed diffuse reflection infrared Fourier transform spectroscopic (TP-DRIFTS) study

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## Abstract

The non-isothermal desorption of water on alkali-metal cation-exchanged X-type zeolites was investigated by means of temperature-programmed diffuse reflection infrared Fourier transform spectroscopy (TP-DRIFTS). Based on the areas under the DRIFT spectra recorded at temperature intervals of 10 K, the desorption profiles could be calculated. Their shape is principally identical to the desorption curves obtained by conventional TPD (EGD/EGA). Using a numerical regularisation method, desorption energy distribution functions have been calculated. The assignment of several characteristic bands to differently bonded water molecules and explanations for certain observed trends have been given. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Water is an important guest molecule in the pore system of natural and synthetic zeolites [1]. Both adsorptive and catalytic properties of zeolites are strongly determined by their water content. Various methods of thermal analysis (TG/DTG, DTA/DSC, and EGD/EGA) are frequently used for investigations concerning the interaction of water with zeolites of different types and with different cations (see, e.g.

Refs. [2–12]). In a recently published paper, it was shown by means of evolved gas analysis (usually known as temperature-programmed desorption or TPD) that the non-isothermal water desorption at higher temperatures on alkali-metal cation-exchanged X-type zeolites mainly depends on the kind of the extra-framework cations [12]. However, these investigation techniques did not yield information about the adsorbed state of water and/or its alteration during the non-isothermal dehydration. A suitable possibility for in situ observation of adsorbed water on zeolites are infrared spectroscopy techniques (e.g. Refs. [10,13–18]). The special method of temperature-programmed diffuse reflection infrared Fourier transform spectroscopy (TP-DRIFTS) (see, e.g. Refs. [19,20]) allows

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investigations under experimental conditions which correspond to those of conventional thermal analysis studies (e.g. loose powder samples, carrier gas flow). Using this method, it is therefore the aim of this contribution to provide some new insight on the non-isothermal dehydration process on alkali-metal cation-exchanged X-type zeolites.

## 2. Experimental

### 2.1. Zeolites

A commercial NaX zeolite (Chemie AG Bitterfeld/Wolfen, Germany) with an Si/Al ratio of 1.18 was used as starting material for the cation-exchanged samples. Ion exchange was carried out with aqueous solutions of KCl and CsCl at 353 K for 8 h. The degree of cation exchange was determined by means of ICP-AES. Furthermore, LSX zeolites with Li<sup>+</sup> and Na<sup>+</sup> cations produced by Tricat zeolites GmbH (Bitterfeld, Germany) were studied. The micropore volumes were determined by nitrogen adsorption at 77 K. The characteristics of all zeolites are summarised in Table 1.

### 2.2. TP-DRIFTS

All experiments were carried out with a System 2000R spectrometer (Perkin–Elmer) using a Praying Mantis diffuse reflection attachment equipped with a stainless-steel reaction chamber (Harrick) which allows temperature-programmed investigations between room temperature and 723 K in a carrier gas flow (helium, 50 cm<sup>3</sup> min<sup>-1</sup>). The zeolites were equilibrated with water vapour over a saturated Ca(NO<sub>3</sub>)<sub>2</sub> solution in a desiccator. For each experiment, 50 mg of the water-loaded zeolite (granulated,

0.2, . . ., 0.4 mm) were used. All samples were flushed with helium at room temperature for 1 h and then the linear temperature program (5 K min<sup>-1</sup>) was started. The spectra were continuously recorded at a resolution of 4 cm<sup>-1</sup> with an average of 32 scans, in the range between 1400 and 4000 cm<sup>-1</sup>. KBr was used as standard (background). The spectra were recorded at intervals of 10 K; this means that a full measurement consists of a set of 30–40 spectra depending on the investigated zeolite. To test the reproducibility, 2–3 independent measurements were performed on the same zeolite sample. In all cases, they result in identical spectra regarding frequencies and intensities. Since the pre-treatment of the zeolite samples (1-h flushing with helium, at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup> at room temperature) is the same as was used in the previous EGD/EGA study [12], the area under the spectra at room temperature has been used for calibration of water amount.

## 3. Results and discussion

Figs. 1–3 show the DRIFT spectra in the region of OH stretching modes, for clarity, at selected temperatures during the non-isothermal dehydration of the NaX, Li-LSX and CsNaX zeolites. Reversibility of the process can be assumed, because several successive desorption experiments carried out on one probe result in identical spectra at the same temperatures. At room temperature, the spectra of all zeolites only show a broad band at about 3400–3500 cm<sup>-1</sup>, caused by the formation of water clusters in the cavities of the zeolites. At about 460 K, a sharp band of free OH groups and two broad bands at about 3200 and 3400 cm<sup>-1</sup> appear in the spectra of each zeolite. Beside the decrease of the intensities of these three

Table 1  
Zeolite characteristics

| Zeolite | Si/Al | Chemical composition   | Micropore volume (cm <sup>3</sup> g <sup>-1</sup> ) |
|---------|-------|--|---|
| NaX     | 1.18  | Na <sub>88.1</sub> [Al <sub>88.1</sub> Si <sub>103.9</sub> O <sub>384</sub> ]                    | 0.295   |
| KNaX    | 1.18  | K <sub>66.1</sub> Na <sub>22</sub> [Al <sub>88.1</sub> Si <sub>103.9</sub> O <sub>384</sub> ]    | 0.263   |
| CsNaX   | 1.18  | Cs <sub>39.6</sub> Na <sub>48.5</sub> [Al <sub>88.1</sub> Si <sub>103.9</sub> O <sub>384</sub> ] | 0.194   |
| Li-LSX  | 1.01  | Li <sub>93.1</sub> Na <sub>2.4</sub> [Al <sub>95.5</sub> Si <sub>96.5</sub> O <sub>384</sub> ]   | 0.309   |
| Na-LSX  | 1.02  | Na <sub>95</sub> [Al <sub>95</sub> Si <sub>97</sub> O <sub>384</sub> ]                           | 0.290   |

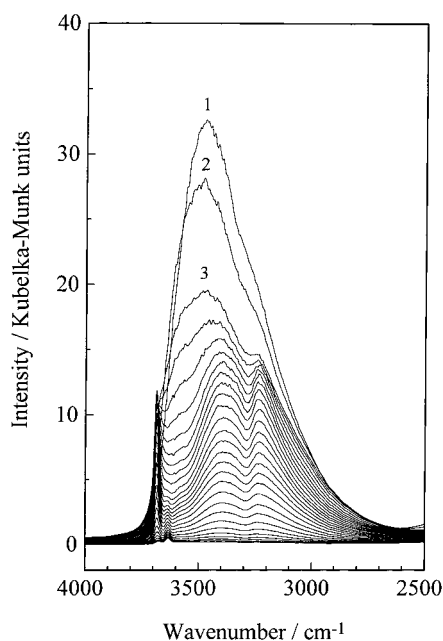


Fig. 1. DRIFT spectra at selected temperatures in the region of OH stretching modes during TPD of water on the NaX zeolite: (1) 303 K; (2) 373 K; and (3) 423–673 K ( $\Delta T=10$  K).

bands, additional sharp OH stretching bands of different intensities appear with decreasing water loading (or increasing temperature).

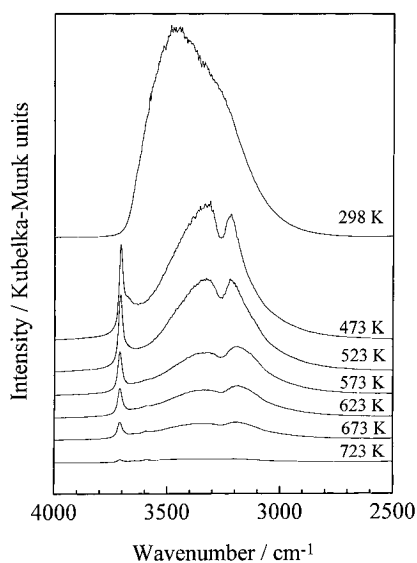


Fig. 2. DRIFT spectra at selected temperatures in the region of OH stretching modes during TPD of water on the Li-LSX zeolite.

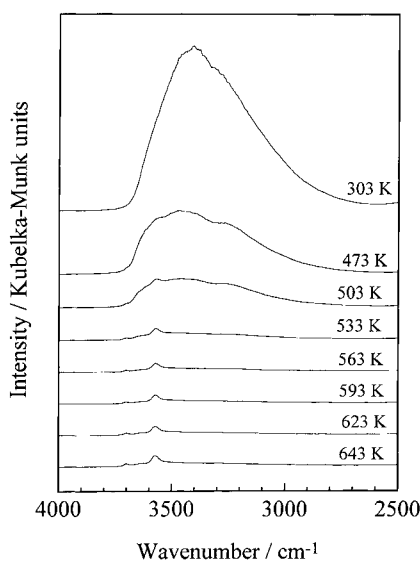


Fig. 3. DRIFT spectra at selected temperatures in the region of OH stretching modes during TPD of water on the CsNaX zeolite.

It can be assumed that the area under the bands at the OH stretching mode region is proportional to the adsorbed amount of water. By integrating the curve over the 2700–3750  $\text{cm}^{-1}$  interval, and building the difference between areas at adjacent temperatures ( $\Delta T=10$  K), a quantity proportional to the amount of water desorbed at the corresponding temperature interval can be calculated. By plotting this quantity against the mean value of the temperature interval, desorption profiles can be obtained. A few examples of these desorption curves are shown in Fig. 4. The desorption profiles possess a pronounced maximum at 428 K (Li-LSX, NaX) and at 418 K (Na-LSX). Two more or less overlapped peaks appear at higher temperatures (from about 460 K), whereby it is characteristic that the highest desorption temperature decreases in the sequence Li-LSX>Na-LSX/NaX. In all cases, the temperature range and the shape of the desorption profiles (relative intensities and number of peaks) agree well with those already obtained by means of TPD (EGD/EGA) of water on these zeolites [12]. The sharp free OH bands at higher temperatures overlap only to a small extent, as can be seen in Figs. 1–3, with the broad association bands. Therefore, it becomes possible to study the desorption course at this temperature range by using the decrease of these band intensities. The desorption profiles were obtained in a

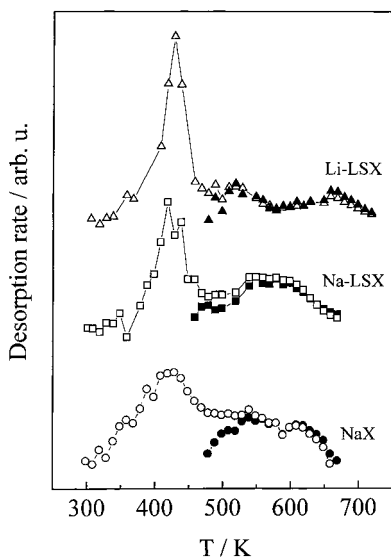


Fig. 4. Desorption profiles of water on Li-LSX, Na-LSX and NaX zeolites ( $5 \text{ K min}^{-1}$ ): open symbols, calculated by using the integral absorption of OH stretching modes; and filled symbols, calculated by using the intensity of the sharp OH band at Li-LSX in the range  $3705\text{--}3712 \text{ cm}^{-1}$ ; Na-LSX in the range  $3670\text{--}3680 \text{ cm}^{-1}$  and NaX at  $3688 \text{ cm}^{-1}$ .

manner analogous to that mentioned above. The results are also shown in Fig. 4. It can be clearly seen that these desorption profiles agree with the high-temperature region of the curves for total amount of water.

In order to obtain further information about the course of dehydration, a deeper analysis of the calculated desorption curves has been carried out. For this purpose, a desorption process of the first order [2,3,5,7], with a distribution function  $f(E)$  of the effective desorption energy  $E$  was considered [21,22]:

$$r_d(T) \equiv -\frac{d\theta}{dt} \\ = A \int_{E_{\min}}^{E_{\max}} \theta_{\text{loc}}(E, T) \exp\left(-\frac{E}{RT}\right) f(E) dE$$

Here,  $r_d(T)$  is the observed overall rate of desorption,  $\theta$  the average coverage or loading, and  $A$  an effective pre-exponential factor,  $\theta_{\text{loc}}$  the coverage of adsorption sites with desorption energy  $E$ , and  $E_{\min}$  and  $E_{\max}$  the limits of the desorption energy range. The calculations were carried out by means of the program INTEG, which involves a regularisation method for solving this

integral equation [21,22]. The calculation of the desorption energy distribution requires the knowledge of the pre-exponential factor  $A$ . Using an extended integral equation, the determination of  $A$  is also possible by means of desorption experiments with different heating rates [22]. However, this numerical method requires experimental data of higher precision. Because the calculation of the desorption curves based on the DRIFT spectra is connected with greater uncertainties (estimation of intensity differences of greater temperature steps,  $\Delta T=10 \text{ K}$ ), the use of the extended integral equation does not seem to be reasonable. Therefore, we have used the value  $A=2.5 \times 10^7 \text{ min}^{-1}$  of our previous EGD/EGA study [12,22] which was obtained using comparable experimental conditions (carrier gas flow rate, sample amount and heating rate). In Fig. 5 the calculated desorption energy distributions  $f(E)$  of water on Li-LSX and NaX are presented in comparison with the distribution functions obtained by means of TPD of water [12]. In both cases, the agreement of the shape of the distribution functions (number and relative intensity of peaks) is obvious. The energy values of the peaks differ at about  $5\text{--}10 \text{ kJ mol}^{-1}$ . This deviation should be caused by the slightly different experi-

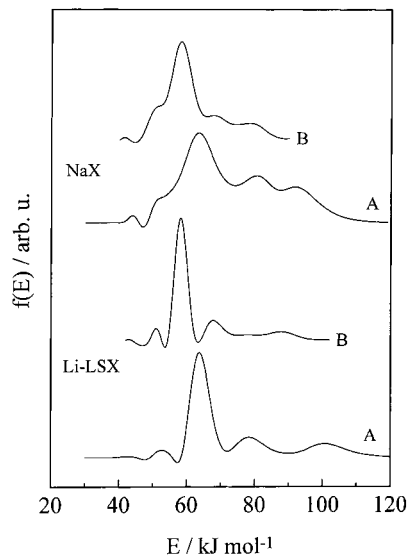


Fig. 5. Calculated desorption energy distribution functions  $f(E)$  of water desorption on Li-LSX and NaX. (A) TP-DRIFTS; and (B) EGA (Ref. [12]).

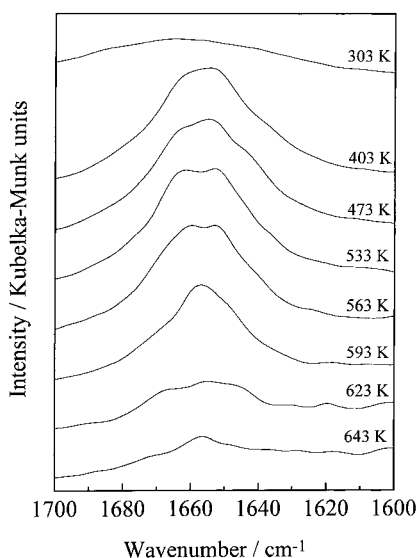


Fig. 6. DRIFT spectra at selected temperatures in the region of HOH bending modes during TPD of water on the NaX zeolite.

mental conditions which mainly influence the value of the effective pre-exponential factor [23] and do not change the shape of the distribution function.

So far it has been shown that the TP-DRIFTS measurements allowed the quantitative recording of non-isothermal water desorption. An additional advantage of this technique is, however, the possibility to derive information about the adsorbed state of the water molecules and/or alteration of these adsorbed states during non-isothermal desorption of water. The DRIFT spectra of the hydrated NaX zeolite are represented in Fig. 6 in the region of bending mode [ $\delta_{(\text{HOH})}$ ] depending on desorption temperature. It can be seen that the relatively broad and non-specific absorption band at about  $1655\text{ cm}^{-1}$  (303 K; that means  $\approx 25$  water molecules per supercage) emerges more and more with increasing temperature while losing intensity. In particular, these spectra can be regarded as proof of molecular adsorbed water.

If structural OH groups were present in the investigated zeolites, one should expect another OH bending vibration at lower wave numbers. On the basis of INS measurements on HY type zeolites, Jobic (Ref. [24]) localises the OH in-plane bending mode [ $\delta_{(\text{OH})}$ ] at  $1060\text{ cm}^{-1}$  while Beck et al. [25] derive similar frequency positions at  $1028$  and  $1057\text{ cm}^{-1}$  from overtones and combination tones. Because of the

strong overlap of  $\delta_{(\text{OH})}$  by the intense SiO stretching modes of zeolite, the  $\delta_{(\text{OH})}$  cannot be detected with usual IR investigations; that means there is no confusion between  $\delta_{(\text{OH})}$  and  $\delta_{(\text{HOH})}$ . In the case of X and Y type zeolites, structural OH groups show two clearly discernible OH stretching modes: the so-called HF band (high-frequency band at  $3640\text{--}3660\text{ cm}^{-1}$  for O1–H bond directed into the supercage, relatively narrow) and the LF band (low-frequency band at  $3545\text{--}3575\text{ cm}^{-1}$  for O3–H bond directed into the sodalite unit, relatively broad) (see, e.g. Ref. [26]). In the region of OH stretching modes (see following figures.), absorption bands at  $\approx 3570\text{ cm}^{-1}$  could be observed in some cases. Due to their sharp and narrow shape, and the absence of HF bands which should be present because of the experimentally and theoretically established distribution of protons over the four framework oxygen positions (O1>O3>O2>O4), these bands cannot be interpreted as LF bands of structural OH groups. Thus, we can conclude that there are no structural OH groups inside of investigated zeolites.

The spectrum of gaseous water shows three fundamentals at  $1595$ ,  $3657$  and  $3756\text{ cm}^{-1}$  which have been assigned to the bending, symmetric and asymmetric stretching modes, respectively. Adsorption of water molecules in cavities of zeolites leads to an asymmetrical perturbation of molecular force field and in consequence of this to a lowering of stretching frequencies mainly caused by interaction of water molecules with cations on the one side and with framework oxygen atoms on the other side as well as to a partial decoupling of OH oscillators (our own normal co-ordinate analyses have shown that even decreasing the OH stretching force constant of only one OH bond by  $0.4\text{ mdyn/\AA}$  (5%) can produce this effect). Thus, one cannot any more speak about asymmetric and symmetric stretchings of water molecule. The DRIFT spectra of water adsorbed on alkali-metal cation-exchanged X-type zeolites shown in Fig. 7 for a loading of one water molecule per supercage can be divided into two regions: the region of OH stretching modes of free OH bonds ( $\nu_{(\text{OH})_{\text{free}}}$ ; relatively narrow bands above  $3500\text{ cm}^{-1}$ ) and the OH stretching modes region of associated OH groups ( $\nu_{(\text{OH})_{\text{ass}}}$ ; broad bands below  $3500\text{ cm}^{-1}$ ). In all cases, at least 2  $\nu_{(\text{OH})_{\text{ass}}}$  and 2–3  $\nu_{(\text{OH})_{\text{free}}}$  can be observed. Assuming an equal distribution of water molecules over the supercages, and the presence of the association bands even at very

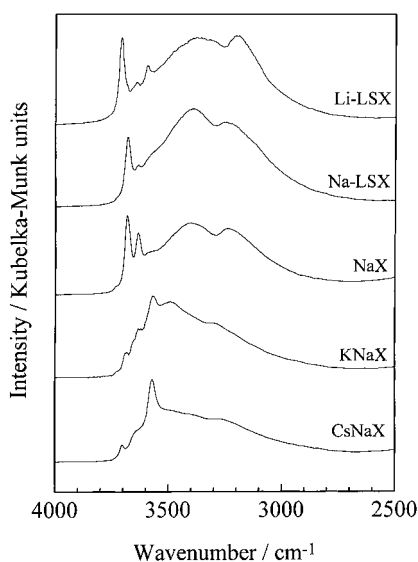


Fig. 7. DRIFT spectra in the region of OH stretching modes of adsorbed water on X-type zeolites (1 molecule H<sub>2</sub>O per supercage).

small loading, the  $\nu_{(\text{OH})_{\text{ass}}}$  should be caused by interaction of water molecules with framework oxygen atoms. X-ray diffraction studies by Kirschhock et al. [27] have shown that the water molecules are always localised between two cations on SIII and SII\* sites. For geometrical reasons, the association of both the OH bonds of a water molecule with nearby located framework oxygen atoms (O1...H–O–H...O1 and O2...H–O–H...O3, respectively) is not probable. Thus, one OH bond of water molecule has to be directed to a framework oxygen atom (O1, O2, O3) and the other one must show into the supercage. Then, water molecules localised in different supercages could interact with different framework oxygen atoms and yield up to 3  $\nu_{(\text{OH})_{\text{ass}}}$  (however, the lower frequency one at about 3200 cm<sup>-1</sup> can also be interpreted as a  $\delta_{(\text{HOH})}$  overtone enhanced by Fermi resonance, see e.g. Ref. [16]). The corresponding  $\nu_{(\text{OH})_{\text{free}}}$  do not show different frequencies. Because of the large mobility of cations inside the zeolite cavities, water-cation clusters with different geometrical structure giving cause to several  $\nu_{(\text{OH})_{\text{free}}}$  can be formed. Such different water-cation clusters can also be considered as the reason for the appearance of two high-temperature peaks in the desorption profiles given in Fig. 4 (Li-LSX: 518 and 658 K, and NaX: 538 and 608 K).

For transition from Li-LSX to NaX zeolite, the  $\nu_{(\text{OH})_{\text{ass}}}$  shifts to higher wavenumbers (3380 to 3406 cm<sup>-1</sup>; 3195 to 3240 cm<sup>-1</sup>) and the intense  $\nu_{(\text{OH})_{\text{free}}}$  to lower ones (3684 to 3711 cm<sup>-1</sup>), respectively. For the following transition to KNaX zeolite the vibrational behaviour changes drastically (Fig. 7). Beside some slight frequency shifts, in particular considerable intensity changes of  $\nu_{(\text{OH})_{\text{free}}}$  are to be observed; in addition the  $\nu_{(\text{OH})_{\text{ass}}}$  are shifted to higher frequencies (3409 to 3491 cm<sup>-1</sup>; 3240 to 3292 cm<sup>-1</sup>). The vibrational behaviour described here remains also in the case of CsNaX zeolite. Assuming the localisation of water molecules always between two cations also in the case of zeolites with different cations (see, e.g. K<sup>+</sup> and Na<sup>+</sup>), an explanation for the vibrational behaviour mentioned above, at least in the case of  $\nu_{(\text{OH})_{\text{ass}}}$  seems likely. As a result of increasing space required of the larger cations (K<sup>+</sup>, Cs<sup>+</sup>), water molecules are displaced more and more from the region of framework oxygen atoms. Thus, the hydrogen bonds are weakened and the  $\nu_{(\text{OH})_{\text{ass}}}$  are shifted to higher frequencies. The increasing partial charge of framework oxygen atoms for larger cations (known from quantum mechanical computations (e.g. Ref. [28]) and electronegativity equalisation method (EEM) results (e.g. Ref. [29])) causing the strengthening of hydrogen bonds is apparently overcompensated by the sterical effect described here.

In Figs. 8–10, the DRIFT spectra of water adsorbed on Li-LSX, NaX, and CsNaX zeolites, respectively, are presented for several higher desorption temperatures (with an increased ordinate scale, see also Figs. 1–3). As can be seen in the case of Li-LSX and NaX zeolites, the intensity of the high-frequency  $\nu_{(\text{OH})_{\text{free}}}$  as well as that one of both the  $\nu_{(\text{OH})_{\text{ass}}}$  decrease with increasing temperature (or decreasing water loading). Both, the weak bands at 3642 and 3601 cm<sup>-1</sup> (Li-LSX) and also the more intense band at 3635 cm<sup>-1</sup> (NaX) are not involved in this decrease of intensity. In the case of CsNaX zeolite, the intensity of all bands decreases in the same extent. As can be seen from the temperature behaviour represented in Figs. 8 and 9, both the  $\nu_{(\text{OH})_{\text{ass}}}$  are connected with the high-frequency  $\nu_{(\text{OH})_{\text{free}}}$ , that means, these absorption bands are related to water molecules bound in the same way. The bands of the free OH groups  $\nu_{(\text{OH})_{\text{free}}}$  are shifted to lower wavenumbers compared to gaseous water and they become more discerned with increas-

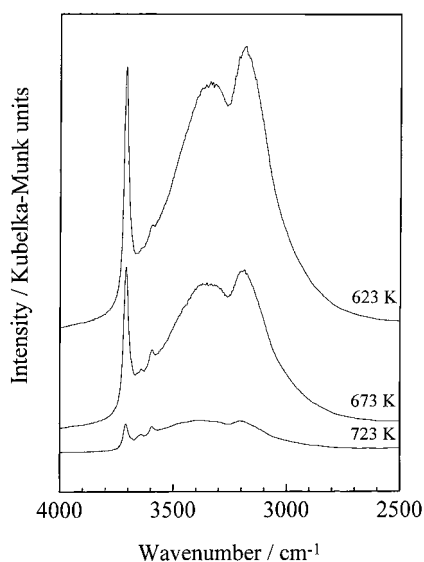


Fig. 8. DRIFT spectra in the region of OH stretching modes during TPD of water on Li-LSX at higher temperatures.

ing temperature. This interpretation is supported by the temperature behaviour of bands in the bending vibration region. The corresponding band of  $\delta_{(\text{HOH})}$  consists of two peaks whose intensity ratio changes, with increasing temperature, in all investigated zeo-

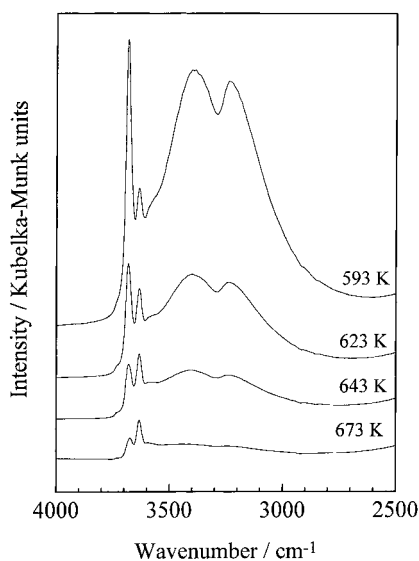


Fig. 9. DRIFT spectra in the region of OH stretching modes during TPD of water on NaX at higher temperatures.

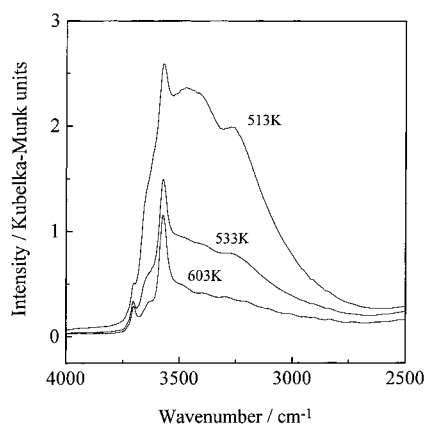


Fig. 10. DRIFT spectra in the region of OH stretching modes during TPD of water on CsNaX at higher temperatures.

lites in the same manner. In Fig. 6 the behaviour of the  $\delta_{(\text{HOH})}$  is shown with increasing temperature in the case of NaX. One could at once notice the change in the intensity ratio of the two main peaks, i.e. at relatively low temperatures the peak at a somewhat lower wave number is most intense, at higher temperatures it is the other peak which has the greatest intensity. This is also the case for Li-LSX and CsNaX zeolites with the only difference being that the change of the intensity ratio becomes visible at about 600 K for the Li-LSX zeolite and at about 500 K for the CsNaX. The two peaks can be regarded as corresponding to two different species of adsorbed water with slightly different H bonds. The one with the stronger H bond gives rise to the peak at higher wavenumbers and should be assigned to stronger bound water compared to the other species.

In conclusion it has to be emphasised that the interpretation of water bands in zeolites regarding structure and bonding of adsorption complexes will be an interesting and challenging problem whose clarification, however, certainly requires further investigations.

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