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Infrared Studies on Water Adsorption Systems with the Use of HDO. II. Na-Y Zeolite

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Infrared spectra of the systems of Na-Y zeolite–H_2O, D_2O, and HDO were measured. It was shown that there are three types of adsorbed water in the zeolite–water system. Type I: adsorbed in a state in which two hydroxyl bonds are highly non-equivalent; it gives absorptions at 3695, 3400, and 1645 cm^{-1}, and is the same type as that on the Molecular sieve 13X.[1] Type II: adsorbed in another state in which the bonds are nearly equivalent; it gives bands at 3610, 3540, and 1645 cm^{-1}. Type II was more resistant to dehydration than Type I, and was irreversible for the back-adsorption of a small amount of water at room temperature, whereas Type I was almost completely reversible. Type III was observed for back-adsorption under this condition; it gives bands at 3635, 3500, and 1655 cm^{-1}. Type III can be transformed into Type II by heat treatment at a temperature which varies depending on the amount of adsorbed water. The other bands were assigned as follows: Bands at 3750 and 3645 cm^{-1} correspond to stretching of surface structural OH, and that at 3240 cm^{-1} to overtone deformation of adsorbed water. The sites of adsorbed water molecules of Types I and II were discussed.

In a previous paper[1] one of the authors showed that HDO could be effectively used for the IR analysis of water adsorption systems through the analysis of the system on Molecular sieves 13X and 4A. In the present paper, the water adsorption system on Na-Y zeolite will be analyzed by employing the same technique.

A number of IR studies have been published on the water adsorption system.[2–5] However, not all of the bands have been clarified, and there are some disagreements about the spectra observed and their assignments. The purpose of the present work is to analyze the spectra of the system on the basis of information obtained from a new technique employing HDO. The sites of the adsorbed water molecules will also be discussed.

Experimental

Linde Molecular sieve SK-40 (UNION SHOWA Co., Ltd.), which is a synthetic Na-Y zeolite, was used as the sample. Major components of the material were SiO_2 63.5, Al_2O_3 23.5, and Na_2O 13.0 in wt %. The crystallinity of the sample was confirmed to be sufficiently high by the measurements of X-ray diffraction and surface area (903 m^2/g, N_2).

Two IR spectrophotometers, a DIGILAB Model 15-B FTS and a JASCO Model 402-G, were used for recording the spectra. The latter instrument was calibrated against the former by use of ammonia, water vapor, and hydrogen bromide.

Other materials, apparatus, and procedures were the same as described before.[1]

Results

Spectra for the Desorption Process. The spectra of Na-Y zeolite–D_2O and H_2O systems after being evacuated at various temperatures are shown in Figs. 1 and 2. As seen in the Figs. various bands observed in the spectra of the two systems after the corresponding evacuation treatments can be easily matched with each other. These matching bands will be referred to using the same letters: a, b,···, and g for the spectra of both systems. Frequencies of these observed bands

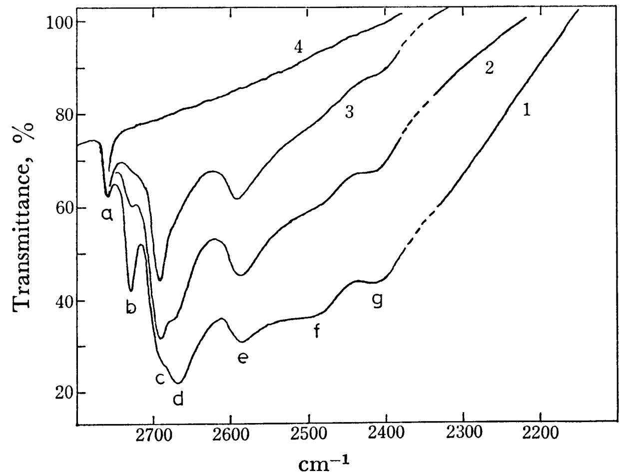

Fig. 1. Spectra of the Na-Y–D_2O system, on the desorption process.
Evacuated for (1) 1 h at 90 °C, (2) 1 h at 120 °C, (3) 30 min at 165 °C, (4) 3 h at 500 °C. "Thickness" of the sample piece was 18 mg/cm^2.

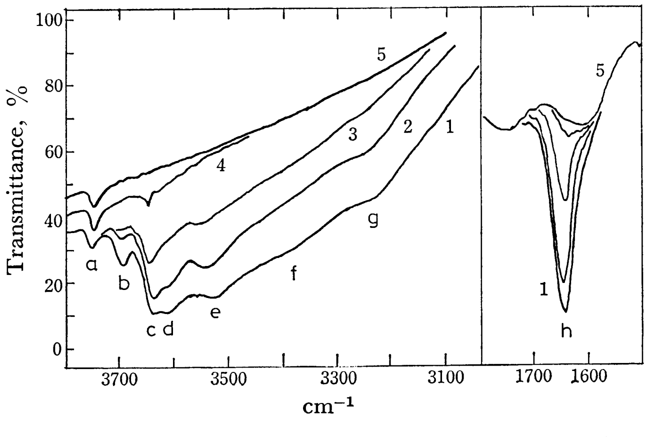

Fig. 2. Spectra of the Na-Y–H_2O system, on the desorption process.
Evacuated for (1) 1 h at 90 °C, (2) 1 h at 120 °C, (3) 30 min at 165 °C, (4) 45 min at 200 °C, (5) 3 h at 500 °C. Sample piece "thickness" 18 mg/cm^2.

Table 1. Summary of the IR bands of Na-Y zeolite-water system

Band symbol	D_2O system (cm^{-1})	H_2O system (cm^{-1})	HDO system (cm^{-1}) Stretching regions OD	OH	Deformation region	Assign
			(1) The desorption process			
a	2760	3750	2760	3750		1)
b	2730	3695	2714	3690		2)
c	2692	3645	2692	3645		3)
d	2668	3610	2647	3600		4)
e	2586	3540	2615	3540		5)
f	2490	3400	2490	3380		6)
g	2405	3240				7)
j				2940		8)
k					1460	9)
n					1422	
h		1645				10)
l					1450	
m					1440	
			(2730)			11)
			(2) The adsorption process			
a	2760	3750	2760	3750		12)
b	2730	3695	2717	3690		13)
o	2675	3635				14)
q			2580	3250		
p	2575	3500				
f	2480	3350	2465	3350		15)
g	2405	3240				16)
j				2960		17)
s		1655				18)
r					1495	
h		1640				19)
k					1460	
n					1422	

1,12), 3): OD(OH) stretching of structural deuteroxyl groups. 2,13), 6,15), 9,19): OD(OH) stretching and deformation of Type-I water. 4), 5), 10): OD(OH) stretching and deformation of Type-II water. 7,16): DOD(HOH) overtone deformation of adsorbed water. 8, 17): Overtone deformation of adsorbed HDO. 11): Arising from D_2O impurity. 14), 18): OD(OH) stretching and deformation of Type-III water.

are summarized in Table 1-(1) together with those of the corresponding bands observed for the HDO system and also with their assignments. The spectra observed for the H_2O system were similar to those reported by Ward,[2] with the exception that the band appearing at 3630 cm^{-1} in his spectra was observed to be clearly separated into two bands at 3645 (c) and 3610 cm^{-1} (d) in our spectra. Bands which were equivalent to these appeared at 2692 and 2668 cm^{-1} for the D_2O system.

Spectra observed for the HDO system in the OD, OH stretching and the HOD deformation regions are shown in Figs. 3 and 4. Those spectra shown in Figs. 3 and 4 were measured after the same evacuation treatments as those performed prior to the measurements of the spectra shown in Figs. 1 and 2, respectively, so that a comparison between the spectra of the D_2O or H_2O system and of the HDO system should be reasonable.

Correlations between the spectra in the OD stretching region of the HDO system and those of the D_2O system were analogous to those between the spectra in the OH stretching region of the HDO system and those of the H_2O system.

As in the case of the Molecular sieve 13X–water system,[1] bands a and c in the spectra of the D_2O or H_2O system appeared at just the same frequencies for the HDO system (bands a′ and c′ in Figs. 3 and 4). Band b shifted toward the lower frequency side by 16 cm^{-1} in the OD stretching region and by 5 cm^{-1} in the OH region for the HDO system. The weak absorption at 2730 cm^{-1} in Fig. 3 arises obviously from the D_2O present in the sample water mixture (about 6.3%). Band g disappeared from the spectra of the HDO system. A new band appeared for the HDO system at 2940 cm^{-1} in the OH stretching region; it can be attributed to an overtone deformation or a combination band of adsorbed HDO, like the band at 2945 or 2910 cm^{-1} which appeared in other zeolite–HDO systems.[1] Bands at 2668 (d) and at 2586 cm^{-1} (e) in the spectra of the D_2O system disappeared from the OD stretching region of the HDO system. Two

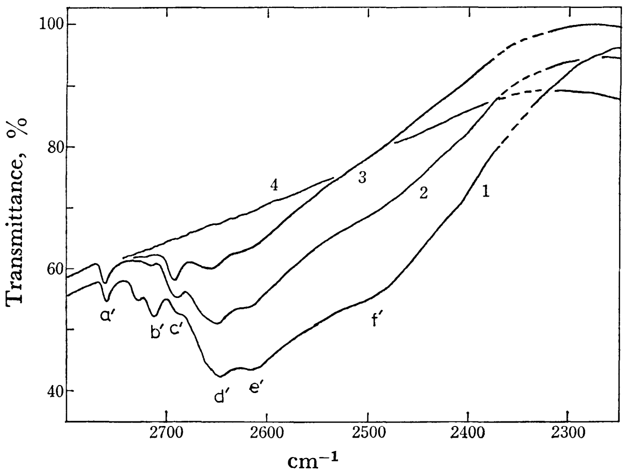

Fig. 3. Spectra of the Na-Y-HDO system in the OD stretching region, on the desorption process. Evacuated for (1) 1 h at 90 °C, (2) 1 h at 120 °C, (3) 30 min at 165 °C, (4) 3 h at 500 °C after exposure to the vapor of H_2O-D_2O mixture of a molar ratio of 3 to 1. Sample piece "thickness" 40 mg/cm^2.

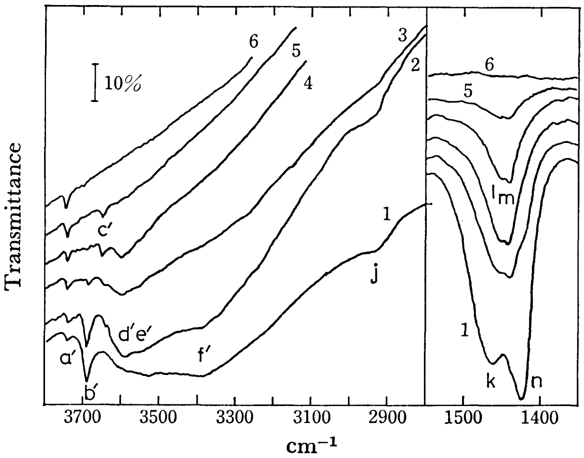

Fig. 4. Spectra of the Na-Y-HDO system in the OH stretching and deformation regions, on the desorption process.
Evacuated for (1) 10 min at 90 °C, (2) 1 h at 90 °C, (3) 1 h at 120 °C, (4) 30 min at 165 °C, (5) 45 min at 200 °C, (6) 3 h at 500 °C after exposure to the vapor of H_2O-D_2O 1 to 5 mixture. The spectra shown in the deformation region were obtained by rationing each observed spectrum against that after 500 °C evacuation of the Na-Y-H_2O system. Sample piece "thickness" was 26 mg/cm^2.

new bands, presumably corresponding to bands d and e, appeared at 2647 (d′) and 2615 cm^{-1} (e′) in the OD stretching region. In the OH region these bands d′ and e′ were detected in the spectra after evacuation at lower temperatures (curves 1 and 2 in Fig. 4) at 3600 and 3540 cm^{-1}, which were nearly the same frequencies as those of d and e in the spectra of the H_2O system. After the evacuation at higher temperatures, however, the band e′ could not be observed, probably because the absorption was weak and broad. In the deformation region four absorptions (k, l, m, and n) appeared at 1460, 1450, 1440, and 1422 cm^{-1} in the HOD deformation region for

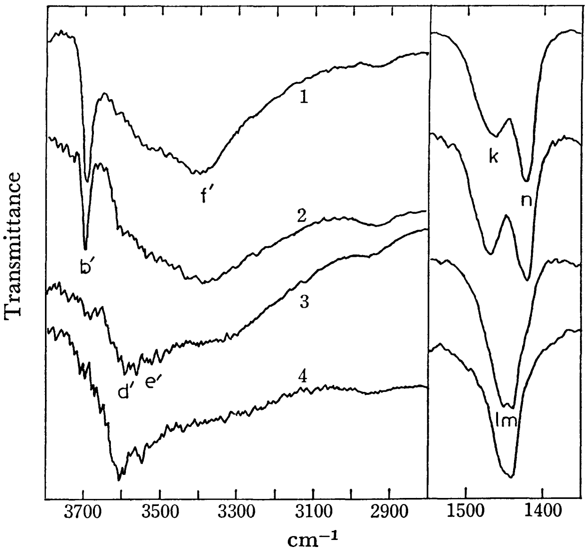

Fig. 5. Ratioed spectra of the Na-Y-HDO system in the OH stretching and deformation regions, on the desorption process. Obtained rationing (1) curves 1 and 2, (2) 2 and 3, (3) 3 and 4, (4) 4 and 5 of Fig. 4. The scale of the intensity is arbitrary as each curve is "auto expanded" into an identical hight in the frequency ranges indicated.

the HDO system, whereas only one at 1645 cm^{-1} (h) was found for the H_2O system.

On evacuation in a series where the evacuation temperature was elevated step by step, the intensity of the bands b and f for the D_2O (H_2O) system and also of the bands b′, f′, k, and n for the HDO system decreased preferentially in the initial steps, followed by the decrease of the bands d and e for the D_2O (H_2O) system and of d′, e′, l, and m for the HDO system. The intensity of band h decreased at a constant rate through the dehydration treatments. This can be seen directly in the ratioed spectra shown in Fig. 5. Those spectra were obtained for the HDO system by calculating the intensity differences between each curve shown in Fig. 4 by use of a computer system included in the FTS-15 spectrometer. Thus, it was suggested that bands b, f, and h for the H_2O (D_2O) system (corresponding bands b′, f′, k, and n for the HDO system) should have the same origin, while bands d, e, and the residual part of h (d′, e′, l, and m) came from another origin.

Spectra for the Adsorption Process. Spectral measurements on the adsorption process were also made for the systems of various kinds of water in the surface coverage of about 0—1.2 mmol/g. The general features of the spectra were almost identical irrespective of the degree of coverage in each of the systems, but were somewhat different from those of the spectra for the desorption process, as is seen in the typical examples shown in Figs. 6 and 7. Differences were found in two regions: one is the region where bands d and e appeared for the desorption process and the other is the deformation region. In the former, two relatively broad bands (o and p) appeared at 2675 and 2575 cm^{-1} for D_2O adsorption, and at 3635 and 3500 cm^{-1} for H_2O adsorption. Each of the former

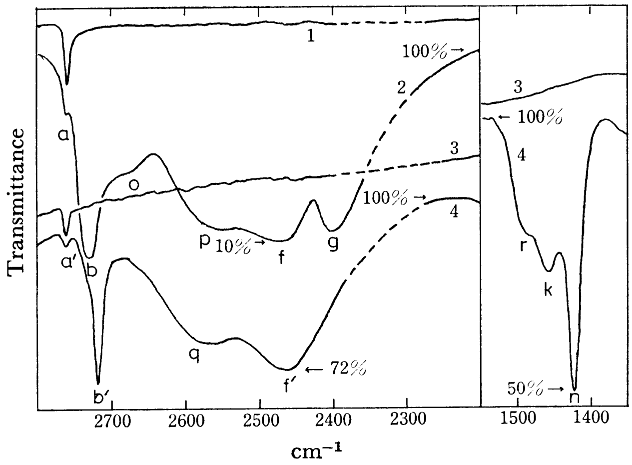

Fig. 6. Spectra of the Na-Y–D_2O and HDO systems in the OD stretching and the HOD deformation regions, on the adsorption process.
(1,3) Evacuated for 3 h at 500 °C, (2) 40 μmol of D_2O, (4) 40 μmol of H_2O–D_2O 7 to 1 mixture were readsorbed. All the curves were obtained by rationing the observed spectra against that after 500 °C evacuation of the Na-Y–H_2O system. Sample piece "thickness" 17 mg/cm^2.

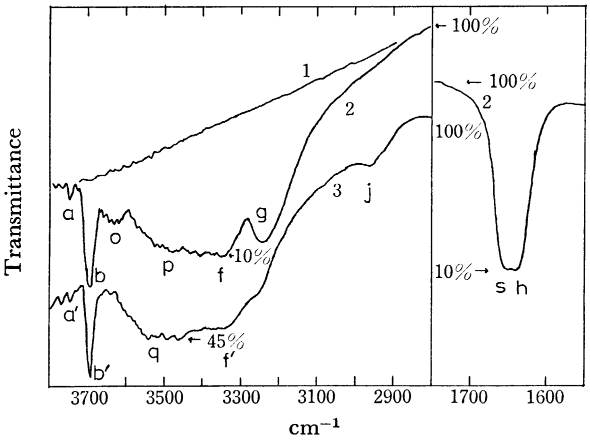

Fig. 7. Spectra of the Na-Y–H_2O and HDO systems in the OH stretching and the deformation regions, on the adsorption process. (1) Evacuated for 3h at 500 °C, (2) 24 μmol of H_2O, (3) 24 μmol of H_2O–D_2O 1 to 5 mixture were readsorbed. Curve 2 in the deformation region was obtained by rationing the observed spectra against that after 500 °C evacuation. Sample piece "thickness" was 17 mg/cm^2.

bands was very weak. For HDO only one broad band (q) was observed in the region around 2580 cm^{-1} for the OD region and around 3520 cm^{-1} for the OH region. Three deformation bands were observed for the HDO system, at 1495 (r), 1460 (k), and 1422 cm^{-1} (n), while two were found at 1655 (s) and 1640 cm^{-1} (h) for the H_2O system.

Observed frequencies of the various bands are summarized in Table 1-(2).

Discussion

Spectra for the Desorption Process. First, bands a and c can be assigned to the stretching vibrations of surface structural OH (OD) groups, while the remaining absorptions b, d, e, f, g, and h are attributable to some vibrations arising from adsorbed water molecules. This is because of the fact that each pair of corresponding bands, one appearing in the H_2O (D_2O) system and the other in the HDO system, of the former group appeared at the same frequency in the corresponding regions of the spectra of the H_2O, D_2O, and the HDO systems, while in the latter group the bands did not appear at the same frequency in at least one region of the spectra.

Thus there is just the same type of adsorbed water (Type I, adsorbed in a state in which its two hydroxyl bonds are highly non-equivalent) in the Na-Y zeolite–water system as the Type WX-I in the Molecular sieve 13X–water system which was reported in a previous paper.[1)] That is, bands b, f, g, and h in the spectra of the present work are apparently attributed to the same vibrations as bands b, e, f, and at 1650 cm^{-1}, respectively, in the spectra of the 13X system. Each pair of these matching bands showed an almost identical behavior with the partial deuteration of the adsorption systems.

Absorptions d and e have been observed and reported only by Ward.[2)] He assumed that they were due to some adsorbed water molecule, but no details were described. Our results in the present experiments support his assignment. Moreover, they give further information on the state of the adsorbed molecules as described below. When a water molecule is adsorbed in a state in which its two hydroxyl bonds are completely equivalent, the molecule is expected to give two stretching bands of ν_3 and ν_1 and one deformation band of ν_2 for H_2O (D_2O), as well as single OH and OD stretching bands which are located between the ν_3 and the ν_1 frequencies and one HOD deformation band for HDO. On the other hand, when the molecule is adsorbed in another state in which the hydroxyl bonds are not equivalent, H_A–O–H_B, it is expected that two OH stretching bands (one is rather characteristic of νOH_A and the other of νOH_B) and a single deformation band arise for H_2O and D-equivalent bands forD_2O. For HDO molecules in this state four stretching bands: νOH_A, νOH_B, νOD_A, and νOD_B and two deformation bands: δH_AOD_B and δH_BOD_A will occur. The degree of frequency difference between the vibrations νOH_A and νOH_B or between the two D-equivalent bands, as well as between the two deformation bands, will be larger, the larger the degree of the non-equivalency between the two hydroxyl (deuterioxyl) bonds. In the present results, bands d' and e', presumably corresponding to the $\nu OD_A(\nu OH_A)$ and the $\nu OD_B(\nu OH_B)$ of the HDO, appeared close to each other, being located between the frequencies of the corresponding bands d and e of the D_2O (H_2O). Thus, bands d and e can be assigned to the ν_3 and ν_1 vibrations of water molecules adsorbed in a state in which its two hydroxyl bonds are nearly equivalent (Type II). The result in the deformation region also supports this assignment. Two deformation bands (l and m) were observed to be very close to each other, with a difference of only

10 cm^{-1}, for the Type II adsorbed HDO. The corresponding difference was 38 cm^{-1} for the Type I water, in which the difference between the two OD stretching bands was 224 cm^{-1}. Hence, such a small difference of 10 cm^{-1} will be reasonable for the Type II water, in which the difference between the two OD stretching bands was 32 cm^{-1}.

In a previous paper$^{1)}$ it was suggested that the weak absorption at 3590 cm^{-1} (D-equivalent band at 2645 cm^{-1}) in the spectra of the Molecular sieve 13X–water system was due to some type of adsorbed water molecule, but with no details. It is almost certain that the band arose from a similar type of adsorbed water to the present Type II water.

Spectra for the Adsorption Process. From a comparison with the spectra of the desorption process, the deformation band at 1640 cm^{-1} (h) in the H_2O system should correspond to those at 1460 (k) and 1422 cm^{-1} (n) of the HDO system, and the new band at 1655 (s) to that at 1495 cm^{-1} (r). This speculation is in harmony with the appearance of the bands in the stretching regions. Bands b, f, and g did appear at almost the same positions as those in the spectra of the desorption process; moreover, they showed similar behavior to those of the latter bands for the partial deuteration. On the other hand, bands o and p for the H_2O (D_2O) system and q for the HDO system are quite different in their spectral aspects from bands d, e, d′, and e′ of the desorption process. These facts indicate that the Type I water is almost reversible while the Type II is not, for readsorption of a small amount of water at room temperature.

The new bands o (3625, D-equivalent 2675 cm^{-1}), p (3500, D-2575 cm^{-1}), and s (1655 cm^{-1}) would be assigned to the ν_3, ν_1 and ν_2 vibrations of water adsorbed in some state with its hydroxyl groups equivalent (Type III), and bands q at 3520 and 2580 cm^{-1} and r (1495 cm^{-1}) to the OH stretching, OD stretching, and the deformation of the corresponding HDO molecules.

The state of these adsorbed molecules is obviously different from that of the Type II water, even if somewhat similar to it. In order to investigate this irreversibility a simple experiment was carried out. After 0.83 mmol/g of D_2O was back-adsorbed at room temperature, the sample piece, *in situ*, was heated up to 95 °C or 200 °C once, and then cooled slowly down to room temperature. It was found that the treatment at 200 °C gave rise to a great change in the spectrum, giving a similar spectrum to that on the desorption process with bands at 2694 (c), 2674 (d), and 2590 cm^{-1} (e). This indicates the rearrangement of the adsorbed water molecule, probably from the Type III to the Type II, and the formation of certain structural hydroxyl groups caused by dissociation of adsorbed water. And also it suggests that the Type II water is more stable than the Type III water. However, in the 95 °C treatment no spectral change occurred, whereas our spectra for the desorption process were obtained by 10 min of evacuation at 90 °C after the dried sample piece was saturated with water vapor. Thus, it is suggested that the occurrence of the rearrangement of adsorbed water and the formation of the hydroxyl groups depend on the degree of surface coverage as well as temperature. The details can not be known without further experiments.

Sites of Adsorbed Water Molecules. Mutual comparison of the results obtained for the present Na-Y zeolite and for the Molecular sieves 13-X (Na-X zeolite) and 4-A (Na-A zeolite)$^{1)}$ makes it possible to discuss the sites of adsorbed water molecules.

Type I and Type II water existed on both the zeolites of Na-X and Na-Y, while on the Na-A zeolite Type I water could not be found. The single main type of adsorbed water observed on the Na-A is regarded to be similar to the Type II water in its symmetry.

Under such a condition of much lower surface coverage,$^{6)}$ it is almost sure that the adsorption of water molecules occurred mainly on the zeolitic cations in such a manner that the lone pair electrons of the water oxygen atom are attracted to the positive charge of the cations, whether or not the hydrogen atoms are hydrogen bonded to the negatively charged oxygen of the zeolite lattice. Hence, it will be reasonable that the variety in the modes of adsorption should be discussed in connection with the kind of cation sites.

It is well known that the crystal structures of zeolites X and Y are essentially identical, but differ only in the number of their cations and the strength of the electrostatic force field around the cations. According to Rabo *et al.*,$^{7)}$ there are three kinds of possible cation sites, S_I, S_{II}, S_{III}, in the zeolite structure. The number of each site is 16, 32, and 48, respectively, for a X type zeolite of which the ratio of Al and Si equals unity. These sites are occupied by exchangeable cations, fully or partially, depending on the type of the zeolite. On the other hand, Na-A zeolite$^{8)}$ has another structure. But it includes sodalite cages similarly to the structure of the Na-X or Na-Y. There are two kinds of sites, S_1 and S_2, in the type A zeolite. For the Na-A, 12 Na cations are required per unit cell for electrical neutrality, of which 8 Na cations occupy the former site and the remaining 4 Na the other site.

Among those five kinds of sites, the site S_I can be ruled out of consideration because the cations positioned at that site will not be able to accept any adsorbate due to its small space. Site S_{II} is regarded to be similar to site S_1. Both are situated on the center of the six-membered rings of the sodalite cages facing toward the super cages of the zeolite structure, and have a C_{3v} symmetry in relation to the neighboring lattice oxygens. Site S_{III} is characteristic of zeolites X and Y, which is located on the center of four-membered rings of the sodalite cages and has a symmetry of C_{2v} in relation to the neighboring oxygens. Zeolite A has no such site.

From both the similarity and the differences among the three zeolites in the geometry around the possible cation sites and in the observed spectra, it is suggested that the Type I water is situated on the cations occupying the site S_{III}, whereas the Type II is on those of site S_{II}.

These attributions are supported by a comparison between the intensity of the spectra of each type of adsorbed water and the number of the cations occupying each site, as described below. The relative amount of the Types I and II water on the Na-X and Na-Y zeolites can be estimated from the results shown in the present Fig. 1 or 2 and those shown in Fig. 1 or 2 of the previous report.[1] In that case, the intensity of the spectra of the 13-X water system must be compared with the other after being multiplied by a factor of 1.6, which appears from the differences in the sample thickness and the molecular weight per their unit cells.[9] Then, it can be seen that there is a much smaller amount of Type I adsorbed water on the Na-Y zeolite than on the Na-X. The Type II water is estimated to be present in much the same amount on both zeolites, or at least not so much less on the Na-X than on the Na-Y zeolite, though this is not very clear because of the overlapping of the spectra of the Types I and II water. On the other hand, according again to Rabo *et al.*,[7] the order of preference for cation occupation is $S_I > S_{II} > S_{III}$, which may lead to the conclusion that our Na-X sample (Si/Al=1.23) includes 16, 32, and 38 Na ions per unit cell for the respective sites, while the Na-Y sample (Si/Al=2.3) includes 16, 32, and 10, respectively. That is, the ratios of the cation number positioned on the same site in Na-X and Na-Y are 1:1 for the site S_{II} and 38:10 for the S_{III}. This may be comparable with the relative intensity of the spectral bands described above.

The molar absorptivity for the Type II water appears to be weaker than for the Type I water. This is probably due to the fact that the Type I water is more strongly polarized than the other. It has been shown by Dempsey[10] that the electrostatic force fields around the site S_{III} is some 50% stronger than that around site S_{II}.

It is obscure at present why and in what geometrical arrangements the Types I and II water are adsorbed on the sites, yielding such modes as described before. To answer this question, further experiments with the use of other techniques are necessary.

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9) Thickness of the sample pieces were 12 mg/cm^2 and 18 mg/cm^2 respectively for the Na-X (Molecular sieve 13X) and Na-Y zeolites. Molecular weight of the zeolites per unit cells are 13423 g and 12809 g for Na-X and Na-Y, respectively.

10) Ref. 7, p. 33.