574 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (3), 574—579 (1977) [Vol. 50, No. 3

Infrared Studies on Water Adsorption Systems with the Use of HDO.
I. Molecular Sieves 13X and 4A

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(Received July 12, 1976)

It was shown that the use of HDO molecules in IR studies on water adsorption system is advantageous for obtaining information as to whether 1) a band arises from the surface structural hydroxyl groups or from adsorbed water molecules, 2) a band arises from an overtone bending vibration, and 3) water molecules are adsorbed in a state of its two hydroxyl bonds being equivalent. The bands in the spectra of Molecular sieves–H_2O systems were assigned as follows. I) 13X–H_2O system. Bands at 3752, 3685, and 3647 cm^{-1} correspond to surface structural OH, bands at 3697, 3360, and 1650 cm^{-1} to asymmetrically adsorbed water molecules, band at 3230 cm^{-1} to overtone bending vibration of the same molecules. The band at 3590 cm^{-1} was found to arise from some other type of adsorbed water molecules. II) 4A–H_2O system. Bands at 3500, 3400, and 1660 cm^{-1} correspond to symmetrically adsorbed water molecules, band at 3280 cm^{-1} to overtone bending vibration of the same molecules. Another type of adsorbed water was suggested to be present.

Infrared spectroscopy has been widely employed in studies on surface and adsorbed species. However, analysis of the spectra has not always been easy to carry out. This is due to inevitable characteristics of the spectra of adsorption systems, such as the specific complexity of the spectra and the lack of means of spectral observation over a wide frequency range masked by strong absorption by adsorbents.

Thus, additional information from other sources is desirable. As an example, the use of partially deuterated compounds is considered to be effective. The use of this technique has been made for the spectral study on adsorption systems to some extent.[1] A number of investigations have been carried out on water adsorption systems. However, they were restricted to the measurement of the spectra of H_2O or D_2O adsorption systems. No work seems to have been made with the use of HDO.

In the present work, IR absorption spectra of hydroxyls and adsorbed water on Molecular sieves 13X and 4A are analyzed by the use of HDO. Although assignments of the spectral bands of these systems have been made to a certain extent,[2–14] more direct and conclusive evidences for the assignments are obtained by the use of the present technique.

Its applicability to other molecular adsorption systems will be suggested.

Experimental

Materials. Linde molecular sieves 13X and 4A (GASUKURO Ind. Co., Ltd.) were used. The crystallinity and purity of these materials were confirmed to be of a sufficiently high by X-ray diffraction analysis. The surface area of the 13X sieve was 717 m^2/g. In order to obtain extremely fine powder samples for IR experiments, the materials were ground in an agate motor with a small amount of water, and then suspended in deionized water. The particle size of the fine powders was found to be less than 1μm in diameter by electron microscopic observation. D_2O (E. Merck, Darmstadt) of 99.75% in purity and deionized-distilled H_2O were used for IR experiments after being degassed.

Apparatus and Procedure. A JASCO Model 402-G IR spectrophotometer and a Pyrex glass cell were used for recording the spectra. The cell was essentially similar to that designed by Angell *et al.*[6] In order to prevent the contamination of the sample pieces by grease vapor, a Teflon greaseless valve was fixed directly to the top of the cell. The exchange of sample pieces was made by cutting and re-fixing the arm part of the cell.

The sample powders were pressed into disks under a pressure of 2.5 tons/cm^2, and then the disks were cut into pieces of 1×2 to 2.5 cm to fit the cell windows. The "thickness" was 12—80 mg/cm^2.

After the sample pieces had been set in the cell, they were evacuated at 500 °C for at least 3 h prior to experiments. Before the addition of each type of sample water for IR measurements, the surface of the sample as well as the inner wall of the cell were washed by the following procedure. The sample was exposed at room temperature to the saturated sample water vapor, and then pumped out at 180—200 °C for 10 min. This procedure was repeated five times. Finally, it was evacuated at 500 °C for 3 h. Spectral observation confirmed that the washing was sufficient. In the case of measurements of H_2O–adsorbent systems on a new sample piece, washing was omitted.

The experiments related to HDO were carried out in the presence of H_2O and D_2O. By mixing H_2O with D_2O at a molar ratio of a to b, HDO is obtained under the coexistence of other water in a ratio of about H_2O: HDO: $D_2O=a^2$: $2ab$: b^2.

All the spectra were measured at room temperature. Spectra on the desorption process were observed after the pretreated sample piece was first exposed to the saturated sample water vapor and then evacuated at various temperatures. Spectra on the adsorption process were measured by dosing small amounts of sample water at room temperature successively after the sample piece was evacuated at 500 °C.

The measurements were carried out mainly in the OD stretching region in place of the OH stretching region, since the former is not only higher in transparency but also flatter in background owing to the lack of weak absorption bands arising from the water vapor in the air.

Results

13X–Water System. *D_2O, H_2O Systems*: The spectra of 13X–D_2O and H_2O systems were measured for a comparison of the results with those of the HDO system (Figs. 1 and 2). The spectra observed were similar to those published.[17] On evacuation at 90 °C six absorption bands were observed at 2756, 2727, 2682, 2645, 2470, and 2395 cm^{-1} in the D_2O system, (these

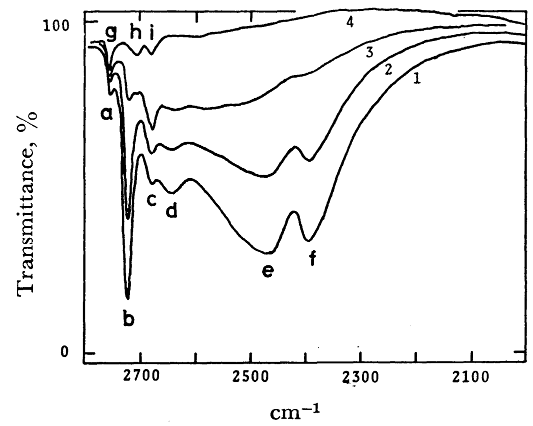


Fig. 1. Spectra of 13 X–D_2O system.
Evacuated for (1) 1 h at 90 °C, (2) 1 h at 120 °C, (3) 20 min at 170 °C, (4) 2 h at 500 °C. "Thickness" of the sample piece was 12 mg/cm^2.

bands as well as the corresponding bands in other systems will be referred to as a, b, c, d, e, and f). In the H_2O system the six bands corresponding to those in D_2O system were at 3752, 3697, 3645, 3590, *ca.* 3360, and 3230 cm^{-1}. In the latter system a single HOH bending vibration band was observed at 1650 cm^{-1}. Elevation of the evacuation temperature gave rise to a decrease in the intensity of all these bands except for a and c. After the final evacuation at 500 °C, three sharp bands remained at 2756, 2708, and 2683 cm^{-1} in the D_2O system (referred to as g, h, and i, respectively), and in the H_2O system at 3752, 3685, 3647 cm^{-1}.

HDO System: The spectra in OD stretching and bending regions are shown in Fig. 3. In this experiment, an H_2O–D_2O mixture in the ratio 3 to 1 was used except for curve 5, the contents being H_2O 56.3%, HDO 37.5% and D_2O 6.3%. In the number of OD chemical bond, the 75% belongs to HDO and the rest to D_2O. The OH stretching region of this system (Fig. 4) was measured employing another mixture in the ratio $H_2O : D_2O = 1 : 5$. The spectra of OD and OH stretching regions of this system were compared with those of D_2O and H_2O systems, respectively. All the correlations

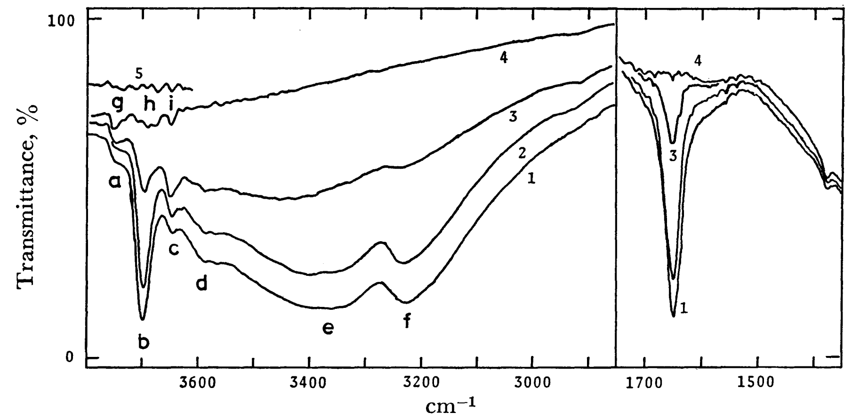


Fig. 2. Spectra of 13X–H_2O system.
Evacuated for (1) 1 h at 100 °C, (2) 1 h at 120 °C, (3) 25 min at 165 °C, (4) 2 h at 500 °C. (5) Empty cell.[16] Sample piece "thickness" 12 mg/cm^2.

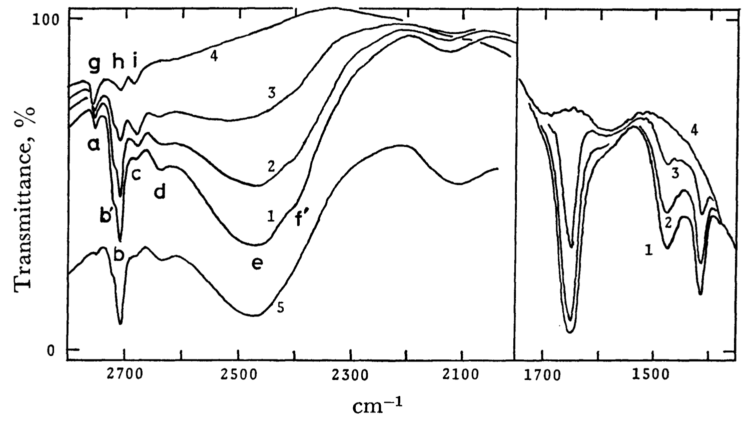


Fig. 3. Spectra of 13X–HDO system in the OD stretching and bending regions.
Evacuated for (1) 1 h at 95 °C, (2) 1 h at 120 °C, (3) 20 min at 165 °C, (4) 2 h at 500 °C after exposure to the vapor of H_2O–D_2O mixture of a molar ratio of 3 to 1, and (5) evacuated for 1 h at 90 °C after exposure to the vapor of H_2O–D_2O 7 to 1 mixture. Sample piece "thickness" 43 mg/cm^2.

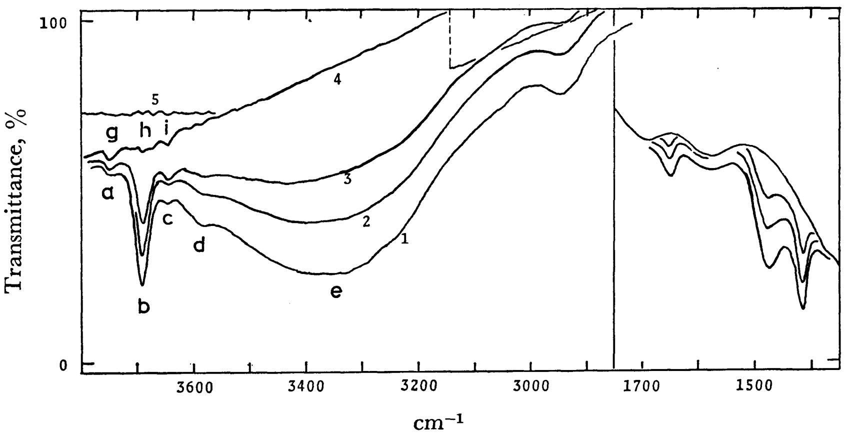


Fig. 4. Spectra of 13X–HDO system in the OH stretching and bending regions. Evacuated for (1) 1 h at 95 °C, (2) 1 h at 120 °C, (3) 20 min at 165 °C, (4) 3 h at 500 °C after exposure to the vapor of H_2O–D_2O 1 to 5 mixture. (5) Empty cell. Sample piece "thickness" 38 mg/cm^2.

between the spectra in the OH stretching region of HDO system and those of H_2O system were analogous to those between the spectra in the OD stretching region of the HDO system and those of D_2O system. The frequencies of the bands in OH stretching regions are parenthesized.

Bands a, c, and e in the spectra of HDO system appeared in the OD stretching region at 2756, 2680, and 2470 cm^{-1} (3750, 3645, *ca.* 3350 cm^{-1}) which were of nearly the same frequencies as those of the D_2O system. However, band b was observed at a distinctly different frequency from that of D_2O system, namely at 2710 cm^{-1} (3690 cm^{-1}). As for band d, even though the difference in frequency was not very great, *ca.* 7 cm^{-1}, the frequency 2638 cm^{-1} was not equal to that of the band in D_2O system. In the OH region, band d was so broad that the difference could not be detected decisively. It should be noted that no band f appeared in the spectra of this system. The fact that the shoulders at 2725 and 2395 cm^{-1} are due to the D_2O molecules contained in the mixed water as "impurity" was confirmed from another experiment, *viz.* the spectra after the adsorption of sample water followed by evacuation at 100 °C were measured in a series where the D content of the sample water was changed step by step from 0 to 100 atom %. The results showed that the intensities of both shoulders change in proportion to the D content. The spectrum in the OD stretching region obtained by the use of $H_2O:D_2O=7.1:1.0$ mixed water is shown in Fig. 3, curve 5. A band somewhat broader and weaker appeared in both stretching regions, at 2945 cm^{-1} in the OH region and at 2120 cm^{-1} in the OD region. The weak absorption bands of g, h, and i were measured in the OD stretching region with a thick sample for the sake of comparison with those in D_2O system. The results showed that the three bands were exactly equal in wavenumber to those in D_2O system, and were 27% in intensity as compared with that of the latter which is almost equal to the D content, 25 atom %, of the mixed water used. In the bending vibration region, three absorption bands were observed at 1650, 1476, and 1415 cm^{-1}. The band at 1650 cm^{-1} is assigned to HOH bending vibration, because its frequency was quite the same as that of pure H_2O system and its intensity decreased with decrease of H_2O content in the mixed water (Figs. 3 and 4). Thus the other two arise from HDO.

The spectra measured on the adsorption process were almost the same as those on the desorption process. However, the intensity of the band d was so weak that the band was hardly observable on the adsorption process in the spectra of any of the systems.

4A–Water System. In this system the spectral measurements were carried out only on the adsorption process.

4A–D_2O, H_2O Systems: In the stretching region of the spectra of D_2O (H_2O) system (Figs. 5 and 6) three main bands were observed at 2578, 2515, and 2427 cm^{-1} (in H_2O system, at 3500, 3400, and 3280 cm^{-1}) and three weak bands at 2760, 2737, and 2645 cm^{-1} (in H_2O system, only the two former bands were detected at 3750 and 3715 cm^{-1}). In H_2O system one bending band was observed at 1660 cm^{-1}. These were similar to those reported by previous authors.[7,8]

4A–HDO System: The spectra obtained in the OD stretching and bending regions employing an H_2O–D_2O

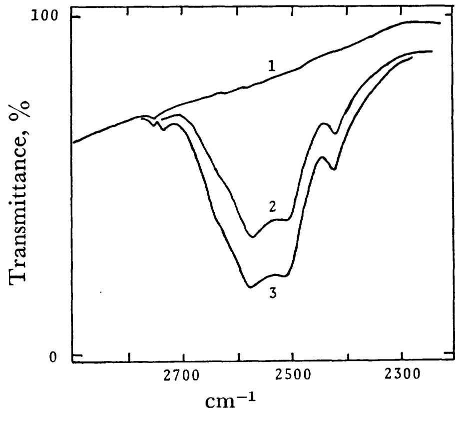


Fig. 5. Spectra of 4A–D_2O system.
(1) Evacuated for 3 h at 500 °C, (2) 9 μmol, (3) 18 μmol of D_2O readsorbed. Sample piece "thickness" 30 mg/cm^2.

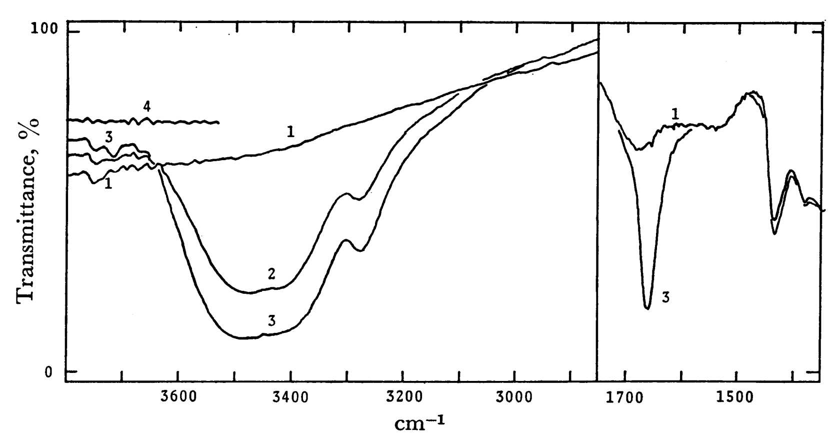


Fig. 6. Spectra of 4A–H_2O system.
(1) Evacuated for 3 h at 500 °C, (2) 9μmol, (3) 18 μmol of H_2O readsorbed. (4) Empty cell. Sample piece "thickness" 15 mg/cm^2.

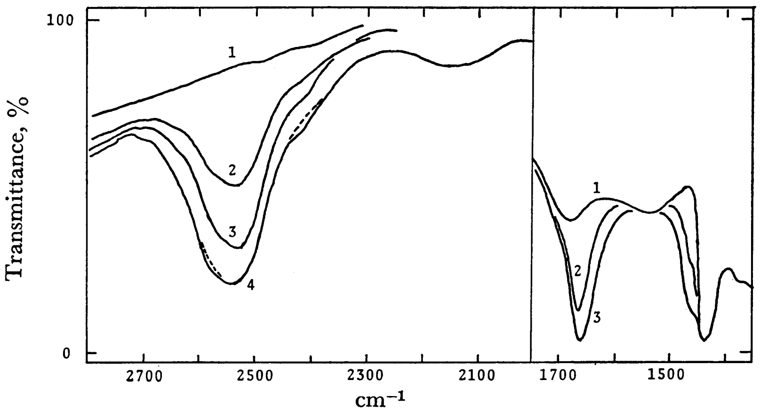


Fig. 7. Spectra of 4A–HDO system in the OD stretching and bending regions.
(1) Evacuated for 3 h at 500 °C, (2) 18 μmol, (3) 36 μmol, (4) 54 μmol of H_2O–D_2O 3 to 1 mixture were readsorbed. Sample piece "thickness" 30 mg/cm^2.

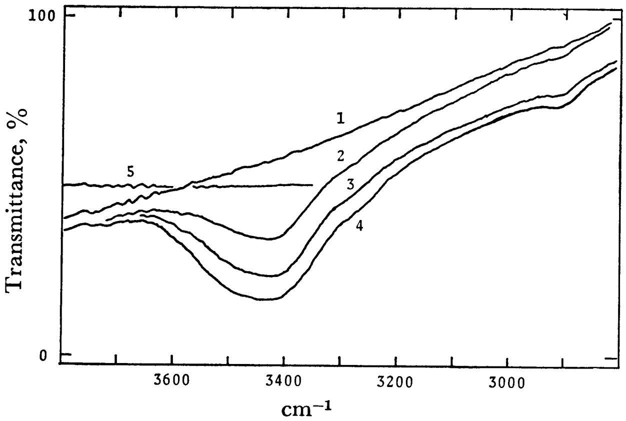


Fig. 8. Spectra of 4A–HDO system in the OH stretching region.
(1) Evacuated for 3 h at 500°C, (2) 18 μmol, (3) 36 μmol, (4) 54 μmol of H_2O–D_2O 1 to 5 mixture were readsorbed. (5) Empty cell. Sample piece "thickness" 30 mg/cm^2.

mixture in the ratio 3 to 1 and those in the OH stretching region employing another mixture in the ratio 1 to 5 are shown in Figs. 7 and 8, respectively. In each stretching region, a main single OD or OH stretching band of symmetric shape appeared at a frequency of 2530 or 3420 cm^{-1}. Their positions are located between two strong stretching bands appearing in the spectra of D_2O or H_2O system. A weak band was observed at 2705 cm^{-1} in the OD stretching region but not the fitting band in the OH region. As in the case of 13X–water system a new band was observed in each stretching region at 2140 cm^{-1} in the OD region and at 2910 cm^{-1} in OH region. Both bands at 2427 cm^{-1} in D_2O system and 3280 cm^{-1} in H_2O system disappeared from each corresponding region of the spectra of HDO system. Swellings around 2580, 2420 cm^{-1} (Fig. 7) and 3500, 3280 cm^{-1} (Fig. 8) arise obviously from D_2O or H_2O present in the water mixtures. Only one HOD bending band appeared at 1465 cm^{-1}. The 1660 cm^{-1} band corresponds to HOH bending vibration as previously described.

Table 1. Summary of the IR bands of molecular sieves–water systems

Band sign	D_2O system (cm^{-1})	H_2O system (cm^{-1})	HDO s–stem (cm^{-1}) Stretching regions OD	HDO s–stem (cm^{-1}) Stretching regions OH	HDO s–stem (cm^{-1}) Bending region	As-sign
		[13X–water System]				
a (g)	2756	3752	2756	3750		1)
b	2727	3697	2710	3690		2)
c (i)	2682	3645	2680	3645		3)
d	2645	3590	2638	3590		4)
e	2470	3360	2470	3350		5)
f	2395	3230				6)
h	2708	3685	2708	3685		7)
				2945		8)
		2120				9)
		1650			1476 1415	10)
b′ f′			(2725) (2395) (2120)		(1650)	11)
		[4A–water System]				
	2760	3750				12)
	2737 2645	3715	2705			13)
	2578 2515	3500 3400	2530	3420		14)
	2427	3280				15)
				2910		16)
		1660			1465	17)
			(2580) (2420) (2140)	(3500) (3280)	(1660)	18)

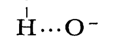
1), 3), 7), 12) OD(H) stretching of structural deuteroxyl groups. 2), 5), 10) Free OD(H) stretching, hydrogen-bonded OD(H) stretching and HOH (HOD) bending of asymmetrically adsorbed water (Type WX–I), respectively. 4), 13) OD(H) stretching of adsorbed water of Types WX–II and WA–II, respectively. 6), 15) DOD(HOH) overtone bending of Types WX–I and WA–I water, respectively. 8), 16) HOD overtone bending or combination of adsorbed HDO? 9) Combination of adsorbed H_2O. 11), 18) Arising from D_2O or H_2O impurities. 14) OD (H) stretching of symmetrically adsorbed water (Type WA–I). 17) HOH(HOD) bending of Type WA–I water.

The observed bands are summarized with their assignments in Table 1.

Discussion

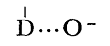
13X–Water System. Discussion has been made as to whether various absorption bands, especially those of h, i, d, and b, arise from surface hydroxyl groups or from adsorbed water molecules.[15] The use of HDO gives more detailed information. If a band arises from the former, the wavenumbers of the corresponding two OH (or OD) vibration bands, one appearing in the H_2O (or D_2O) adsorption system and the other in the HDO adsorption system, should be exactly the same as each other, and if it arises from the latter the wave numbers would not be equal. Thus, the residual bands g, h, and i can be attributed to the stretching vibrations of surface hydroxyl groups, since their corresponding bands appear at the same frequency in the two systems. Bands a and c are also attributable to hydroxyl groups. They would be the same bands as g and i, respectively, because of equal frequency. However, the origin of band b differs from that of h. The fact that band b in HDO system appears in the OD stretching region at a frequency 16 cm^{-1} lower than that in D_2O system (as well as in the OH stretching region 7 cm^{-1} lower than that in H_2O system) indicates that the band does not arise from structural hydroxyl groups but from adsorbed water molecule. Band e is attributed to the OH stretching vibration of the water molecules hydrogen bonded to the surface. The absorption d was reported by Habgood,[5] Ward[9] and also by Kiselev *et al.*[12] However, no assignment was made. Only Uytterhoeven *et al.*[11] attributed the band to OH groups in ions of the type $Me^+(OH)$. However, the results in the present experiments indicate that its origin is not the structural OH groups but a certain type of adsorbed water molecule. Band f was considered by Ward[9] and Abramov *et al.*[14] to arise from the OH stretching of another type of water molecule adsorbed in a different way from the origin of band e. Kiselev *et al.*[12] attributed it to the overtone bending vibration of the water molecules, which are the origin of band e, enhanced by Fermi resonance. Our results support the assignment by Kiselev *et al.* The frequencies of the overtone bending vibrations of HDO would be near 2952 and 2830 cm^{-1} if they appear, since the fundamentals were observed at 1476 and 1415 cm^{-1}. However, since they differ a great deal from the frequency of any stretching vibration of HDO, no resonance would occur. Thus, if the band arises from the overtone bending vibration it would not appear in the spectra of HDO system, or would be only slightly observable at frequencies near 2952 and 2830 cm^{-1}. There is some uncertainty in the attribution of the observed 2945 cm^{-1} band to the overtone bending of HDO molecules. If we suppose that the 2945 cm^{-1} band is the overtone of 1476 cm^{-1} band, we cannot explain the reason why that of 1415 cm^{-1} band does not appear. However, at least the disappearance of band f from the spectra of HDO system is in line with the assignment by Kiselev *et al.* On the other hand, if Ward's assignment is accepted, no reason can be found for the disappearance of the band.

There were two bending vibrations in the adsorbed HDO molecules, but only one in adsorbed H_2O. This supports the schematic structure of water adsorption originally proposed by Bertsch and Habgood[3] (I). If the structure is adopted, the adsorbed HDO molecules would take either of the two forms onto the surface by equal chance as illustrated in (II)-a and (II)-b, then the adsorbed HDO molecules as well as the H_2O



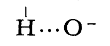
$$\begin{array}{l} {}^{H}\diagdown O\cdots Na^+ \\ \quad\ \, | \\ \quad\ \, H\cdots O^- \end{array}$$

(I)



$$\begin{array}{l} {}^{H}\diagdown O\cdots Na^+ \\ \quad\ \, | \\ \quad\ \, D\cdots O^- \end{array}$$

(II)-a



$$\begin{array}{l} {}^{D}\diagdown O\cdots Na^+ \\ \quad\ \, | \\ \quad\ \, H\cdots O^- \end{array}$$

(II)-b

molecules should yield the bending vibrations in accordance with the observed results. This adsorption model also supports the experimental fact on the stretching vibration of the adsorbed molecules. There were two OH (OD) stretching vibration bands, one of free OH (OD, band b) and the other of hydrogen bonded OH (OD, band e), in both spectra of H_2O (D_2O) and HDO systems.

4A–Water System. First, the band at 3280 cm^{-1} in the spectra of H_2O system (at 2427 cm^{-1} in the D_2O system) is assigned to the overtone bending of adsorbed H_2O (D_2O) in the same manner as in the discussion on 13X–water system, although there remains some doubt in attributing the 2910 cm^{-1} band in HDO system to the overtone of 1465 cm^{-1} band in analogy of the case of 13X–water system. Then, the existence of two strong OH (OD) stretching bands, presumably corresponding to the ν_3 and ν_1 vibrations, and one bending band in the spectra of H_2O (D_2O) system suggests that there exists only one adsorbed species with two equivalent hydroxyl bonds. This is also supported by HDO adsorption experiment. If HDO molecule is adsorbed in this manner, OH, OD stretching bands and HOD bending band arising from the adsorbed molecule should all be single. This is in line with the observed results.

The weak bands at 2737 and 2645 cm^{-1} (Fig. 5) are possibly assigned to the ν_3 and ν_1 vibrations of another adsorbed D_2O molecule, which may fit the origin of the weak 2705 cm^{-1} band in HDO system (Fig. 7). However, the reason is not clear why the bands corresponding to them, except for at 3715 cm^{-1} in H_2O system, do not appear in the OH regions.

Bands at 2945, 2120 cm^{-1} in 13X–HDO System and at 2910, 2140 cm^{-1} in 4A–HDO System. The frequency ratios of each couple of bands, 1.39 and 1.36, seem to suggest that they arise from OH and OD stretching vibrations of HDO molecules adsorbed. However, these assignments contradict the fact that the frequencies are too low and no band corresponding to them could be detected in the spectra of H_2O or D_2O adsorption systems. In order to investigate the origin of these bands the spectra of pure H_2O, D_2O and mixtures of D_2O and H_2O were measured in liquid phase. The results show that there is a band at 2140 cm^{-1} in the spectrum of pure H_2O, its intensity decreasing with a decrease in H_2O content. No band around 2945—2910 cm^{-1} was detected in the spectrum of either pure H_2O or D_2O, but a band appeared in the spectra of mixed waters at 2920 cm^{-1}. Simultaneously, an HOD bending band was observed at 1450 cm^{-1} in the latter spectra. From a comparison of the spectra of liquid water with those of adsorption systems, the band at 2120 or 2140 cm^{-1} is considered to arise from a combination band of adsorbed H_2O molecules existing in the mixed water. The band at 2945 or 2910 cm^{-1} can be attributed to a overtone bending or a combination band of adsorbed HDO molecule.

The present technique is widely applicable to spectral analyses of adsorption systems including XH_n type molecules, with the use of partially deuterated $XH_{n-1}D$ or XHD_{n-1} molecules. It is applicable, in some cases, to the compounds including the atomic groups of $-XH_n$ type.

The author thanks Dr. Toshio Sato for his helpful advice and Mr. Okio Nishimura for his assistance in electron microscopic techniques.

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15) Refs. 3—6, 9, 10, 12.

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17) Refs. 4, 5, 8, 9, 13.