

Diffuse Reflectance IR Study of Molecular Hydrogen and Deuterium Adsorbed at 77 K on NaA Zeolite Part 2. Overtone, Combination and Vibration-Rotational Modes and Thermodesorption from NaA Zeolite

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(Received December 12, 1997; accepted June, 8, 1998)

DRIFT / Hydrogen / Deuterium / Adsorption / Thermodesorption / Zeolites / NaA

The DRIFT spectra of NaA zeolite loaded with hydrogen or deuterium at 77 K were investigated by Fourier transform IR spectroscopy in the ranges of fundamental stretching, combination, overtone of stretching and vibration-rotational modes. Concomitantly *in situ* thermodesorption (TD) of the probe molecules was carried out in the temperature interval of 77–200 K. Combination of DRIFT and TD measurements provided a better resolution of the spectra and facilitated their assignment and interpretation. Thus, the existence of two types of hydrogen or deuterium adsorption could be confirmed, viz. of a more strongly adsorbed form held by sodium cations in the eight-membered windows and a more weakly adsorbed one attached to the sodium cations residing in the six-membered windows of the structure.

IR-Spektren von NaA-Zeolith wurden nach Beladung mit Wasserstoff oder Deuterium bei 77 K mit Hilfe der diffusen Reflektions-Fourier-Transform-IR (DRIFT)-Spektroskopie in den Bereichen der Fundamental-Streckschwingungen, der Kombinationsschwingungen und der Obertöne von Streckschwingungen sowie der Schwingungs-Rotations-Moden untersucht. Dabei wurden gleichzeitig *In-situ*-Thermodesorptions (TD)-Messungen der Sondenmoleküle H₂ and D₂ im Temperaturintervall von 77 K bis 200 K durchgeführt. Die Kombination von DRIFT- und TD-Experimenten führte zu einer wesentlichen Verbesserung der Auflösung in den Spektren und erleichterte die Zuordnung und Interpretation der Banden. Auf diese Weise konnte das Vorliegen zweier Arten von Wasserstoff- bzw. Deuterium-Adsorptionskomplexen sichergestellt werden: Der stärker gebundene Adsorp-

tionskomplex der Sondenmoleküle H_2 bzw. D_2 beruht auf einer Wechselwirkung mit den Na^+ -Kationen in den 8-Ring-Fenstern, der schwächer gebundene auf einer Wechselwirkung mit den Na^+ -Kationen in den 6-Ring-Fenstern der Struktur.

1. Introduction

The application of IR to detect the perturbation of adsorbed molecules provides important information on, e.g., cation distribution in zeolites [1–5]. Indeed, in our previous publication [6] a low-temperature diffuse reflectance IR study of hydrogen and deuterium adsorption on NaA zeolite confirmed the existence of two different kinds of sodium ions in the zeolite framework which was earlier concluded from X-ray analysis [7]. The sodium cations in the centres of the eight-membered rings of the zeolite structure (sites II) represent the stronger sites of hydrogen or deuterium adsorption at low pressure. Their interaction with H_2 or D_2 gives rise to H–H (or D–D) stretching frequencies of 4077 (2927) cm^{-1} (here and below the figures for deuterium are given in brackets). On the other hand, adsorption on weaker sites, which are represented by sodium ions in the six-membered windows of the sodalite cages, predominates at higher hydrogen or deuterium pressures and results in higher stretching frequencies of adsorbed molecules (2939 cm^{-1} for deuterium). Due to the poor resolution, the corresponding stretching bands for the weaker form of hydrogen adsorption were not resolved.

The stretching bands of hydrogen or deuterium adsorbed on both types of sites are associated with high- and low-frequency satellites which, similar to the previous interpretation of Refs. [1, 6], were attributed to vibrations of adsorbed molecules relative to sodium cations. Such an assignment was confirmed by the experimentally observed isotope effects and agrees with the larger separation between the high- and low-frequency satellites for the stronger form of hydrogen or deuterium adsorption in comparison with a smaller separation of the satellites for the weaker form of adsorption. The additional low intense high-frequency bands separated from the stretching bands by several hundreds of wavenumbers were attributed to the vibration-rotational transitions of adsorbed para- and ortho-hydrogen or deuterium.

The present paper presents further evidence of these conclusions obtained by low-temperature thermodesorption of hydrogen and deuterium from NaA zeolite as monitored by IR diffuse reflectance (DRIFT) spectroscopy for different adsorption sites of hydrogen or deuterium.

2. Experimental section

Similar to the procedure described previously [6], the samples of NaA zeolite were pre-evacuated for 4 hours at 673 K and a pressure of ca. $1.3 \times$

10^{-3} Pa in a quartz glass cell which was used for the IR measurements. Then, hydrogen (99.999 vol%) or deuterium (99.7 wt%) from Messer Griesheim (Düsseldorf, Germany) were adsorbed at 77 K and an equilibrium pressure of 27 kPa.

The diffuse reflectance IR (DRIFT) spectra were recorded at 77 K in presence of gaseous hydrogen or deuterium with a Fourier transform IR spectrophotometer (Perkin Elmer model 2000) supplied with a home-made diffuse reflectance attachment [6]. During the thermodesorption measurements, the optical cell with the zeolite was placed in a quartz glass Dewar flask and cooled with vapour of boiling liquid nitrogen with a continuous temperature control by a digital thermometer (Lauda model R 42/2).

The cell was connected with a grease-free all-stainless steel vacuum line and evacuated by a turbomolecular pump. The amount of the zeolite in the cell (about 0.5 g) was large enough to allow for measurements of the pressure changes resulting from desorption of hydrogen or deuterium at different temperatures by means of a membrane-type pressure gauge. In a typical experiment, the time of heating the sample from 77 to 200 K was ca. 50–60 min. During hydrogen thermodesorption the IR spectra were recorded with a resolution of 4 cm^{-1} at each of the selected intermediate temperatures. The number of scans during these measurements was 100 or 200, whereas recording of the spectra at each of the temperatures did not require more than 3–5 min.

The DRIFT spectra of adsorbed hydrogen or deuterium were presented in relative units without Kubelka-Munk transformation. The spectra were corrected for the background created by the zeolite. For this purpose we used the ratio of the intensities of the light scattered by the samples loaded with adsorbed hydrogen or deuterium to the light reflected by the evacuated zeolite.

The differential spectra were presented as a ratio of the spectrum at a given temperature to the spectrum recorded in the next measurement at somewhat higher temperature. This allowed us to obtain both the spectrum of the gas desorbing from the zeolite in the given temperature interval and that of the molecules remaining on the surface in the adsorbed state. The accuracy of detection of the peak maxima was ca. $\pm 1\text{ cm}^{-1}$ for the well-resolved bands and ca. $\pm 5\text{ cm}^{-1}$ for the weak bands or poorly resolved shoulders.

3. Results

The initial spectrum of hydrogen adsorbed on NaA zeolite at 77 K and a high pressure of 27 kPa is depicted in Fig. 1. It is completely consistent with that one reported earlier [6]. The spectrum contains the main band from the H–H stretching vibrations at 4087 cm^{-1} with three poorly re-

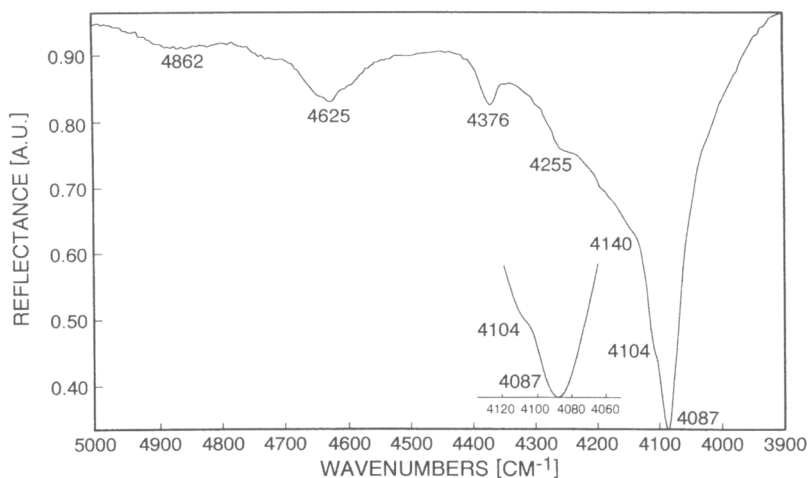


Fig. 1. A DRIFT spectrum of hydrogen adsorbed on NaA zeolite at 77 K and a pressure of 27 kPa.

solved shoulders at 4104, 4140 and 4255 cm^{-1} . The additional weaker high-frequency bands with separations from the main stretching band of several hundreds wavenumbers were earlier ascribed to the vibration-rotational transitions of adsorbed para- and ortho-hydrogen.

The pressure change during thermodesorption of hydrogen from NaA zeolite is shown in Fig. 2. The main part of hydrogen is removed from the surface in the temperature interval of 110–190 K. Due to the poor resolution, the desorption curve does not exhibit any distinct steps which could be related to two different forms of hydrogen adsorption as reported earlier. These forms, however, are clearly indicated by the diffuse reflectance spectra of Fig. 3 which were recorded during thermodesorption and show the significant advantage of combining DRIFT and TD (see also below). In this case, however, no background correction was carried out.

Between 77 and 110 K only a very small fraction of hydrogen is removed from the surface, and the IR spectrum remains essentially unchanged. The most considerable changes occur in the temperature range from 120 to 150 K, where approximately one half of initially adsorbed hydrogen desorbs from the zeolite. This resulted in a decrease in the intensity of the bands and in a shift of the maximum of the main stretching band from 4087 to 4080 cm^{-1} . At higher temperatures of desorption the high-frequency shoulders disappear, and the bands from satellites of the stronger form of hydrogen adsorption at 4168 and 4008 cm^{-1} are clearly resolved (see also Fig. 4). Above 170 K the shape of the spectrum remains un-

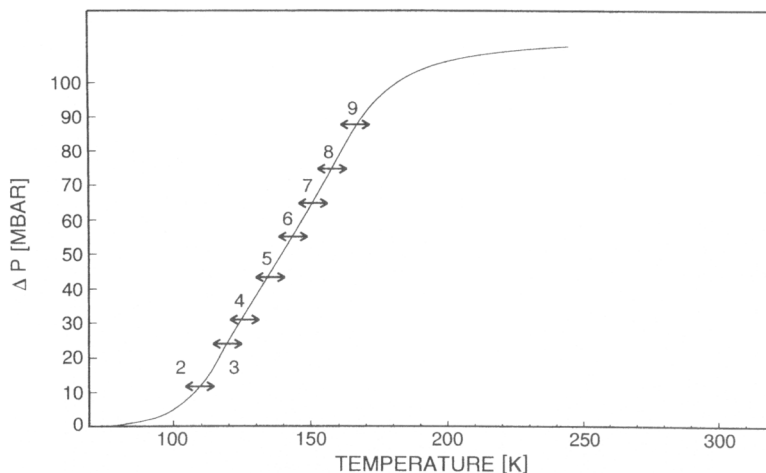


Fig. 2. Increase of hydrogen pressure in hPa during thermodesorption of hydrogen from NaA zeolite at different temperatures; the initial pressure of hydrogen was equal to 27 kPa; arrows indicate the temperature intervals during which the spectra were run.

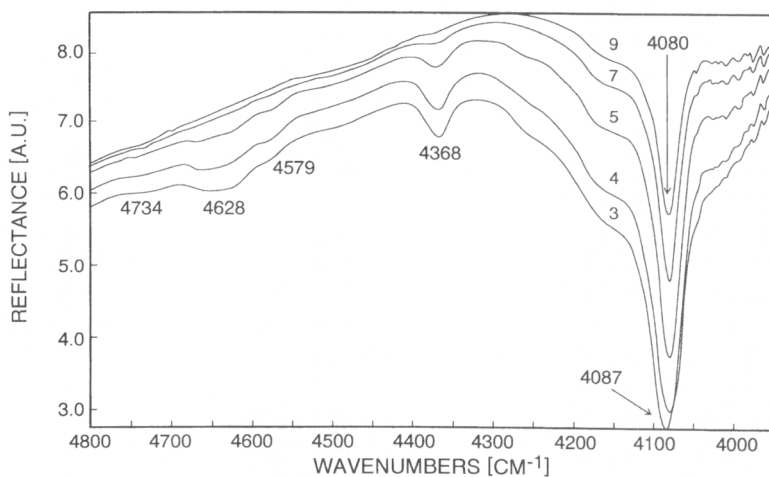


Fig. 3. A set of DRIFT spectra obtained during thermodesorption of hydrogen from NaA zeolite in the same experiment as were the data on pressure change presented in Fig. 2; 3) 115–125 K; 4) 125–135 K; 5) 135–145 K; 7) 150–155 K; 9) 165–170 K.

changed, whereas the intensity of the lines continues to decrease. Finally, at 180–190 K the spectrum becomes very weak in accordance with the desorption curve which also indicates the end of hydrogen desorption.

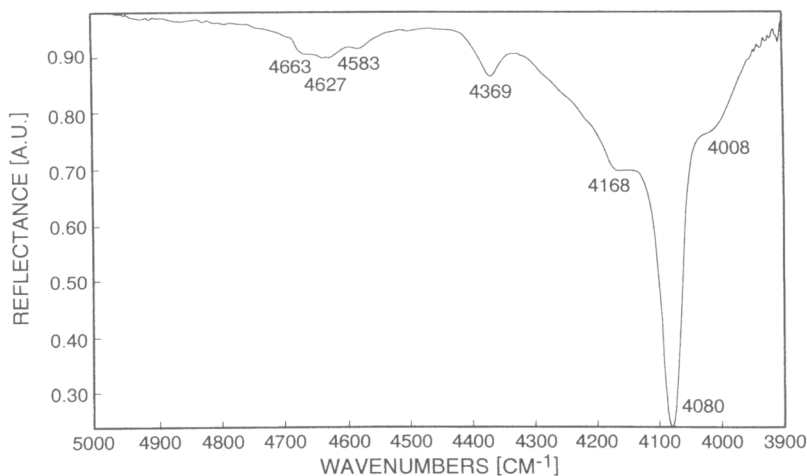


Fig. 4. A DRIFT spectrum of hydrogen more strongly held by NaA zeolite at temperatures above 150 K.

It is certainly not surprising that, after baseline correction, the spectrum of adsorbed hydrogen recorded in the upper temperature interval of desorption (Fig. 4) is identical to that reported earlier for the stronger form of hydrogen adsorption at low pressures [6]. The thermodesorption experiments, however, allowed a much better resolution of the spectrum of the more weakly adsorbed hydrogen which is removed from the surface at low temperatures.

For this purpose we used the differential spectra which represent the spectra of hydrogen or deuterium desorbing from the surface in a given temperature interval. Such a spectrum obtained for the temperature interval of 110–130 K is depicted in Fig. 5. It demonstrates a much better resolution of the satellites and permits a more precise measurement of the separation between them for the weaker form of hydrogen adsorption, viz. 74 cm^{-1} . In addition, the position of the main stretching band at 4093 cm^{-1} in the differential spectrum is slightly shifted toward a higher wavenumber. This also indicates a difference between the IR spectra of weaker and stronger forms of hydrogen adsorption.

The obtained results also provide a better understanding of the high frequency shoulders of the main stretching band shown in Fig. 1. The shoulder at 4104 cm^{-1} most likely belongs to the unresolved signal of the stretching vibrations of the more weakly adsorbed hydrogen, whereas the shoulder at 4140 cm^{-1} indicates the corresponding high-frequency satellite.

The differential spectra of the weaker and the stronger forms of deuterium adsorption are displayed in Figs. 6 and 7, respectively. Generally,

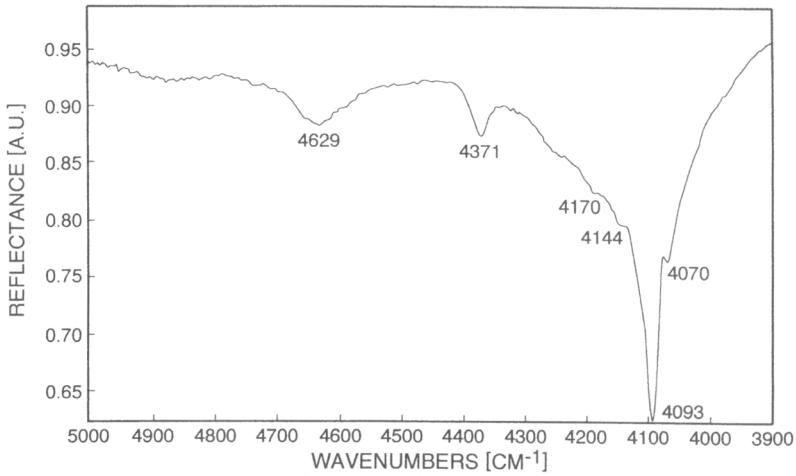


Fig. 5. A differential DRIFT spectrum of hydrogen desorbing from NaA zeolite in the temperature interval 110–130 K.

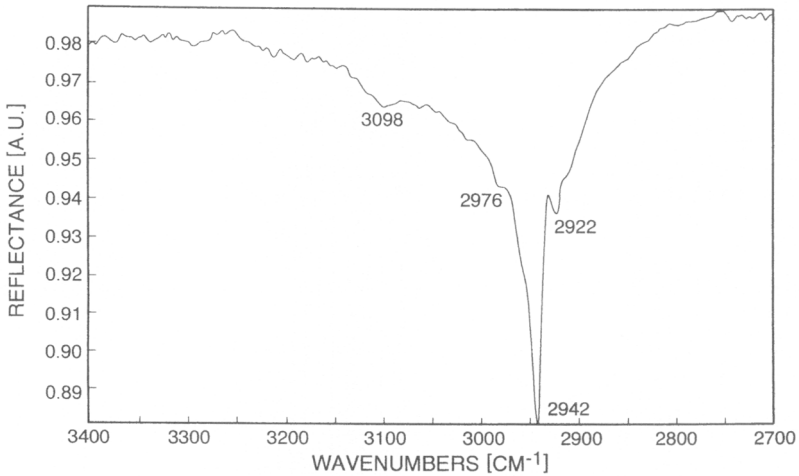


Fig. 6. A differential DRIFT spectrum of deuterium desorbing from NaA zeolite in the temperature interval 110–130 K.

they also demonstrate a much better resolution of the main stretching band and the satellites than the previously reported spectra recorded at different pressures [6].

The above-mentioned two different forms of deuterium adsorption are also clearly seen in the overtone spectra obtained during thermodesorption

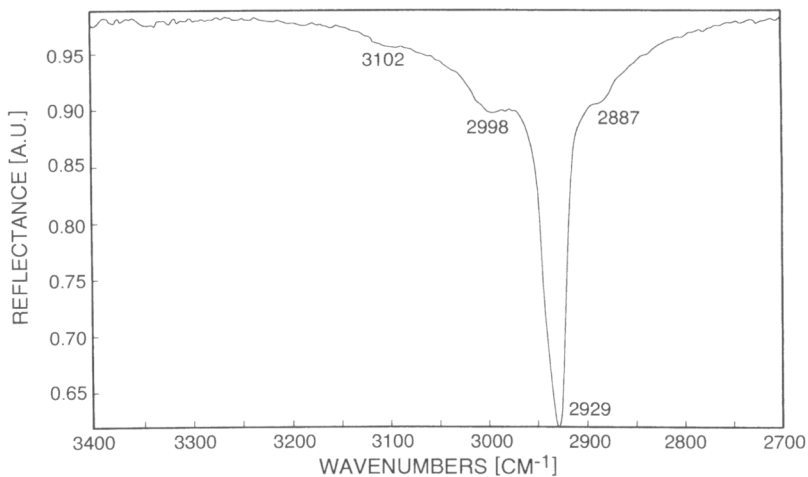


Fig. 7. A DRIFT spectrum of deuterium more strongly held by NaA zeolite at temperatures above 150 K.

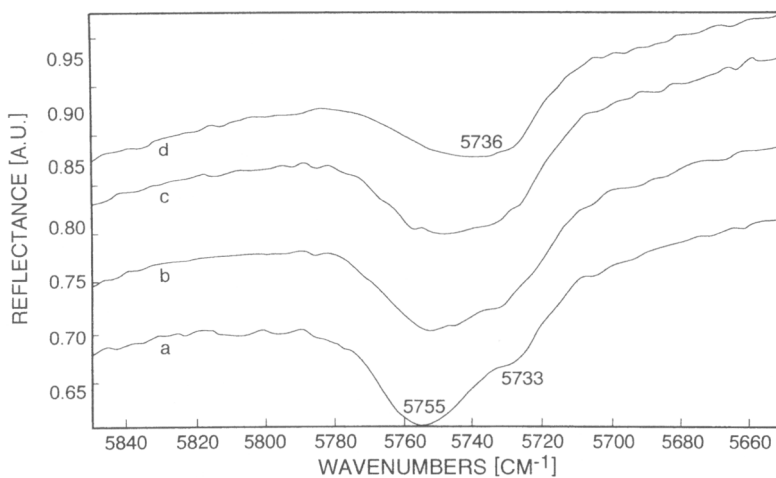


Fig. 8. Overtone DRIFT spectra of deuterium adsorbed on NaA zeolite at different temperatures: a) 120–130 K; b) 140–150 K; c) 150–155 K; d) 155–160 K.

which are shown in Fig. 8. The weaker low-temperature form corresponds to the higher frequency of the stretching overtone maximum at 5755 cm⁻¹. In accordance with the above results, it predominates below 140 K. At

Table 1. Wavenumbers of IR bands of hydrogen and deuterium desorbing from NaA zeolite above 77 K at the initial pressure of 27 kPa.

Assignment	Position/cm ⁻¹		Isotope effect
	H ₂	D ₂	
Weaker forms of adsorption (Na⁺ in the six-membered rings at SI sites)			
stretching vibrations	4093	2942	1.39
hf satellites	4144	2976	
lf satellite	4070	2922	
separation between satellites/cm ⁻¹	74	54	1.37
temperature interval of desorption	77–140 K		
Stronger forms of adsorption (Na⁺ in the eight-membered rings at SII sites)			
stretching vibrations	4080	2929	1.39
hf satellites	4168	2998	
lf satellites	4009	2887	
separation between satellites/cm ⁻¹	160	111	1.44
temperature interval of desorption	130–200 K		

higher temperatures the intensity of this band decreases and, instead of two unresolved bands, only an overtone band due to the high-temperature form of deuterium adsorption is visible at 5736 cm⁻¹.

The data concerning the different forms of hydrogen and deuterium adsorption on NaA zeolite are summarized in Table 1. The positions of the absorption maxima for the stretching vibrations, satellites and for the high-frequency vibration-rotational bands are in a good agreement with those reported earlier [6]. On the other hand, the differential spectra allowed a much better resolution and more precise assignment of the bands originating from the weaker form of adsorption.

4. Discussion

The results of this paper present the following further arguments in favour of two different sites of hydrogen and deuterium adsorption in NaA zeolite:

(i) Two different forms of deuterium adsorption are clearly visible in the overtone D–D stretching spectra of Fig. 8. The weaker form predominates at lower temperatures and is related to the band at 5755 cm⁻¹. By contrast, the stronger form is the only form of adsorption at 160 K and above. It gives rise to the band at ca. 5736 cm⁻¹.

(ii) The thermodesorption DRIFT spectra also allowed us to distinguish between these two forms of hydrogen and deuterium adsorption in

the fundamental stretching region. The positions of the maxima due to the weaker forms are 4093 cm^{-1} and 2942 cm^{-1} for hydrogen and deuterium, respectively. These figures result in an isotope effect, i.e. a ratio of the frequencies, of 1.39 which is close to the theoretical value of 1.41 found for stretching vibrations.

(iii) The thermodesorption study indicated the temperature regions where each form of the adsorption predominates. For the weaker forms of H_2 and D_2 adsorption these are the temperatures below 140 K or, according to Ref. [6], the pressure region above 8 kPa at 77 K. By contrast, the stronger forms of hydrogen or deuterium adsorption predominate at temperatures above 140 K or at equilibrium pressures below 8 kPa at 77 K.

(iv) The weaker and the stronger forms of hydrogen or deuterium adsorption can be also clearly discriminated by different separations between high- and low-frequency satellites. For the stronger forms these separations are about twice as large as for the corresponding weaker forms. Probably, this is the most significant difference between both types of the adsorption which allows to distinguish them much better than the shifts of fundamental frequencies or the positions of the vibration-rotational bands.

Now we will discuss in more detail the nature of the high-frequency bands which were earlier ascribed to the partially hindered rotation of adsorbed hydrogen or deuterium [6]. The main reason for such an assignment was provided by the positions of these bands which are close to, but somewhat lower than the frequencies of freely rotating ortho- or para-hydrogen and deuterium molecules.

The theory of hindered rotation of different fragments in free molecules has been worked out in detail in a number of previously published papers (see, for instance, the reviewing paper Ref. [9]). For adsorbed molecules such information is much more limited. Nevertheless, the partially hindered rotation of adsorbed hydrogen and deuterium was discussed earlier in connection with separation of para- and ortho-hydrogen on aluminum oxide by chromatography [10, 11]. Unfortunately, in those papers only the lowest rotational levels of adsorbed molecules were considered which is not sufficient for discussion of the above DRIFT spectra. In addition, only the van der Waals forces were taken into account neglecting the polarisation of adsorbed molecules by the electric field created by the surface of the adsorbent.

A group theory of partially hindered rotation of different molecules in crystal fields of different symmetry was worked out in Ref. [12]. The obtained results demonstrated that the partially hindered rotation removes the degeneracy of rotational levels and results in a splitting of the corresponding IR bands into several components with positions of the maxima different from those for free rotation. The crystal field theory also indicated that perturbation of a rotational structure is the stronger the lower the symmetry of the field and the higher the hindering barrier. For diatomic molecules

these conclusions were also confirmed by quantum chemical calculations for the hindering force fields of octahedral [13] and tetrahedral [14] symmetry and for molecules adsorbed on a plane with out-of-plane and both out-of-plane and in-plane hinderings [15].

All these conclusions are well consistent with the spectrum of the stronger form of hydrogen adsorption depicted in Fig. 4, where the first rotation-vibrational band is a singlet with a lower separation from the main stretching band (viz. of about 290 cm^{-1}) than for free rotation of para-hydrogen (viz. $6B = 360\text{ cm}^{-1}$). The appearance of the transition for $J = 2$ is in accordance with the results of Poll and Hunt [16], who have shown that this is the analogue of the S transition for a H_2 molecule exposed to the electric field of a point charge which is created in a surrounding solid matrix. In the same study evidence was provided that in the above-indicated situation (H_2 molecule in the electric field of a point charge) even and odd J states do not mix, i.e. ortho- and para-forms are well distinguished. The next vibration-rotational transition is most likely connected with ortho-hydrogen and results in a poorly resolved triplet (at 4663 , 4627 and 4369 cm^{-1}). This clearly indicates the removal of degeneracy of rotational levels of adsorbed hydrogen and, thus, proves its partially hindered rotation.

5. Conclusions

The results of this paper demonstrate that the combination of the spectral data with a low-temperature thermodesorption experiment provides a significant improvement in the resolution of DRIFT spectra of adsorbed hydrogen and deuterium. Moreover, the combination of DRIFT with thermodesorption measurements permits a much better assignment of the bands and interpretation of the spectra. However, it should be stressed that hydrogen, due to its very low mass and low moment of inertia, represents an exceptional case providing the best resolution of the sidebands and of the vibration-rotational structure among the rest of other molecules. This is probably the reason why direct experimental spectral data on hindered rotation or on the vibrations against the surface of zeolites of other adsorbed molecules are so limited (see for example Refs. [1–3]). Therefore, further IR studies of the sidebands and vibration-rotational bands of hydrogen adsorbed on different zeolites may give a very detailed information on the character of motion of adsorbed molecules, on the nature of adsorption sites and on the electric field gradients inside the zeolite micropores.

Acknowledgments

The authors are indebted to Professor Dr. R. Schlögl, Fritz Haber Institute, Berlin and Prof. Dr. Dr. h.c. H. Förster, University of Hamburg, for valuable

discussions. V.B.K. gratefully acknowledges financial support through an Award by the Alexander-von-Humboldt-Stiftung, V.Yu.B. wishes to thank the Russian FFI Foundation (Grant RFFI 97-03-32348) and the Max Plank Society for a generous grant, which enabled him to work for two terms at the FHI.

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