

Drift spectra of adsorbed dihydrogen as a molecular probe for alkaline metal ions in faujasites

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Abstract

DRIFT spectra of dihydrogen adsorbed at 77 K on alkaline–metal forms of X and Y zeolites demonstrate the unique properties of this molecular probe. The spectra provide an information on perturbation of the H–H stretching frequency, on oscillation of hydrogen relative to adsorption sites, and on hindered rotation of adsorbed molecules. The obtained results demonstrate that the perturbed H–H stretching frequency enables to discriminating S_{II} and S_{III} sites inside the zeolite supercages. In addition, for NaY zeolite, the spectral data allow one to draw more detailed conclusions about local distribution of aluminum atoms in the six-membered rings at S_{II} sites. The obtained results also show that the hindered rotation of adsorbed molecules is most sensitive to the nature of cations and to their environment. Finally, the frequency of adsorbed hydrogen oscillations relative to sodium cations is consistent with the diffusion coefficient inside the zeolite micropores previously estimated for NaX by the field gradient NMR. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Dihydrogen; Adsorption; *Ortho*- and *para*-hydrogen; NaX; NaY; DRIFT spectra

1. Introduction

Adsorption separation of hydrocarbons and production of oxygen from air on zeolites is already used by chemical industry for a long time. In this connection, adsorption on these materials of simple gases and hydrocarbons is rather well studied [1]. In contrast, the data on hydrogen adsorption are much more scarce, although this simplest molecular probe has the following important advantages.

(i) Free hydrogen is IR inactive. Therefore, only the molecules perturbed by interaction with adsorption sites can be detected by IR spectroscopy. This eliminates the background created by gaseous hydrogen.

(ii) A dihydrogen molecule is rather small (only 2.9–3.1 Å in diameter). Therefore, hydrogen can be adsorbed even in very narrow micropores. On the other hand, dihydrogen does not penetrate inside the sodalite units of the zeolites framework through the six-membered windows with a diameter of 2.5 Å [1]. This allows to discriminate the sites inside the supercages from those inside the sodalite units.

(iii) The spectral features of dihydrogen are extremely attractive, since this molecule is highly sensitive to perturbation by adsorption sites. In addition, due to the low mass and low moment of inertia, the resolution of vibrational and vibration-rotational IR bands for adsorbed hydrogen is better than that for any other molecule.

(iii) The theory of IR spectra of adsorbed dihydrogen has been extensively worked out. This greatly facilitates the interpretation of the spectral data.

Of course, IR study of adsorbed dihydrogen also presents some experimental difficulties. Among them, the most important one is a weak dihydrogen adsorption, which requires the IR measurements at low temperatures. Another complication consists in a high H–H stretching frequency, which corresponds to the NIR region. However, both these difficulties could be successively overcome by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT spectroscopy) at liquid nitrogen temperature, which is highly sensitive in NIR region. Unfortunately, this technique is still not very common.

Some examples of application of hydrogen adsorption as a molecular probe for the study of zeolites were earlier reported in Refs. [2–11]. Below we will discuss the more recent results obtained in a broader spectral range which provides a more detailed and complete information concerning the nature of adsorption sites and on motion of the adsorbed molecules inside zeolite micropores [11,12].

2. Results and discussion

2.1. DRIFT spectra of adsorbed dihydrogen in a broad spectral range

Let us start with the general features of DRIFT spectra of adsorbed dihydrogen recorded in a broad spectral range. The simplest spectrum of hydrogen adsorbed at 77 K on NaX zeolite expressed in the relative energy units of the light scattered by the sample is presented in Fig. 1a, while Fig. 1b shows the same spectrum after Kubelka–Munk transformation. The main bands in both spectra with the maxima at 4095 cm^{-1} originate from H–H stretching vibrations. This

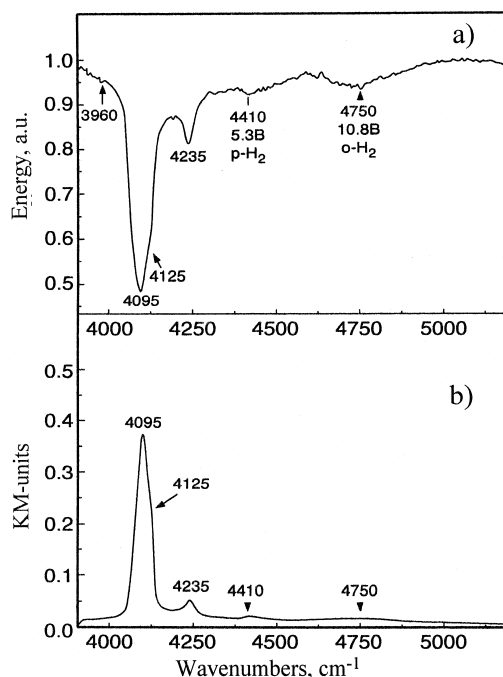


Fig. 1. DRIFT spectra of dihydrogen adsorbed on NaX zeolite with Si:Al = 1.4 at 77 K and 20 kPa. (a) The original DRIFT spectrum expressed in relative energy units of scattered light. (b) The same spectrum after Kubelka–Munk transformation.

wavenumber is by about 65 cm^{-1} lower than that for a free dihydrogen and indicates a perturbation of adsorbed molecules by adsorption sites. (The stronger the perturbation, the larger the low-frequency shift.) The weaker high- and low-frequency satellites are due to the translational motion of adsorbed hydrogen, i.e., to a combination of the stretching vibrations with oscillations of adsorbed molecules relative to adsorption sites. Finally, the very weak broad high-frequency bands in the spectral region above 4300 cm^{-1} correspond to a combination of the stretching vibrations with rotation of adsorbed molecules.

The Kubelka–Munk spectrum of Fig. 1b allows one to estimate the relative intensity of these bands. The intensity of satellites is approximately one order of magnitude lower than that of the main stretching band, while the intensity of the vibration-rotational bands is about one order of magnitude lower than that of

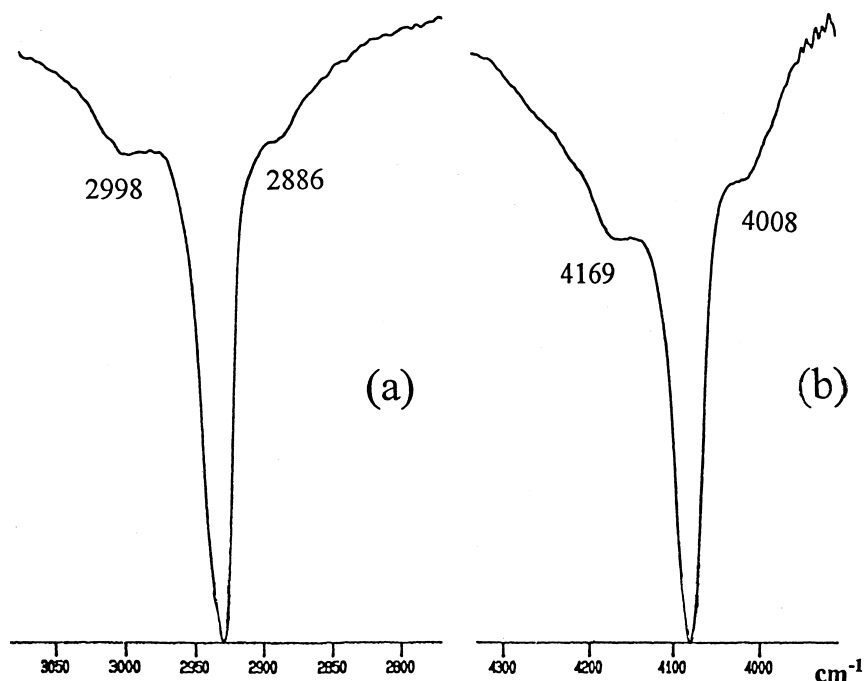


Fig. 2. DRIFT spectra of deuterium (a) and hydrogen (b) adsorbed on NaA zeolite at 120 K at 5 kPa.

satellites. Since the weaker bands are better seen in the original DRIFT spectra, no Kubelka–Munk transformation was performed for the most spectra, which are presented below.

To assign satellites to a combination of stretching vibrations with oscillations of the adsorbed molecules relative to the adsorption sites, we compared the DRIFT spectra of adsorbed

hydrogen and deuterium (Fig. 2). The ratio of separations between satellites in both spectra is practically equal to the square root of the ratio of deuterium to hydrogen masses. This proves the vibrational origin of the satellites. Therefore, they should be ascribed to a combination of the stretching vibrations with oscillations of adsorbed molecules relative to adsorption sites.

Table 1

Positions of DRIFT bands of dihydrogen adsorbed at 77 K and a pressure of 25 kPa on alkaline metal forms of faujasites

Zeolite	Si:Al	Band maxima (cm ⁻¹)			
		Stretching bands (ω_1)	High frequency satellites (ω_2)	$\omega_2 - \omega_1$	Vibration-rotational bands
NaX	1.2	4085 4115 sh.	4225	140	4370, 4450, 4620, 4710, 4825, 4900
NaX	1.4	4095 4125 sh.	4235	140	4410, 4750
LiX	1.4	4100 4125 sh.	4220	120	4390, 4450, 4680, 4850
CsX	1.4	4095 4105 sh.	4235	140	4425, 4465, 4680, 4745
NaY	2.4	4095 4115 4140 sh.	4210	115	4392, 4435, 4610, 4700, 4815, 4910

The frequency of these oscillations can be then obtained as a difference of the frequency of the high-frequency satellite and that of the main stretching band ($\omega_2 - \omega_1$ values in Table 1).

The frequency range of the weaker bands above 4300 cm^{-1} indicates that they belong to a combination of the stretching vibrations with rotation of adsorbed molecules. Indeed, the positions of the energy levels of freely rotating hydrogen are represented by the following well known expression:

$$E_{\text{rot}} = BJ(J + 1) \quad (1)$$

where $B = h^2/8\pi^2I = 59.6\text{ cm}^{-1}$ is the rotational constant of hydrogen.

For *para*-hydrogen the rotational quantum numbers J are exclusively even, while for *ortho*-hydrogen they are exclusively odd. In addition, for both of these modifications, only transitions with $\Delta J = \pm 2$ are possible, since transitions with $\Delta J = \pm 1$ are spin forbidden.

Due to the very large value of B , only the lowest rotational levels with $J = 0$ for *para*-hydrogen and $J = 1$ for *ortho*-hydrogen are populated at 77 K. Therefore, Eq. (1) predicts single vibration-rotational bands for both hydrogen modifications which for free rotation should be separated from the main H–H stretching band by 6 B for *para*-H₂ and by 10 B for *ortho*-H₂. For the spectrum of hydrogen adsorbed on CsX zeolite these values fit well the positions of the experimentally observed lines and indicate a practically free rotation of adsorbed molecules (Fig. 3, Table 1).

To obtain a more direct prove of this assignment, we compared the DRIFT spectra of adsorbed natural hydrogen with *ortho*- to *para*-ratio equal to 3 with the spectra of hydrogen enriched with *para*-modification by about 80% [12]. The latter was obtained by adsorption of conventional hydrogen on activated charcoal at liquid helium temperature with subsequent desorption of *para*-enriched hydrogen at 30–40 K.

Such comparison for hydrogen adsorbed on CsX zeolite is presented in Fig. 3a and b. It is

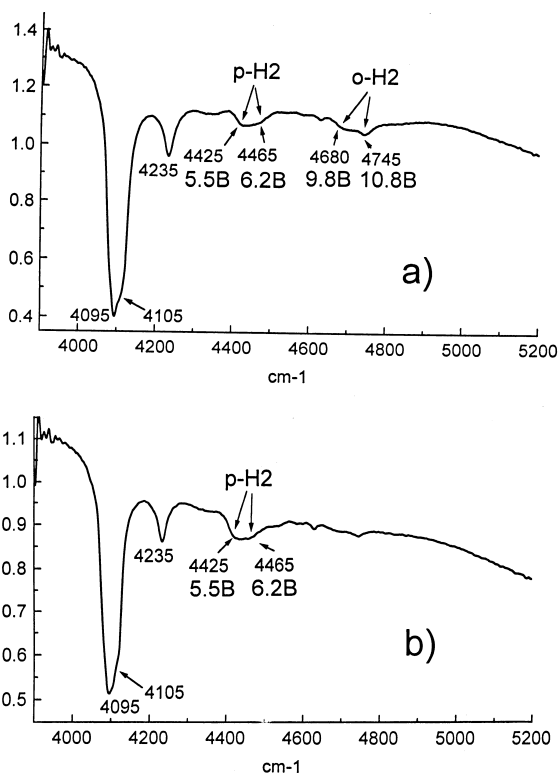


Fig. 3. DRIFT spectra of conventional hydrogen with *ortho:para* ratio equal to 3 (a) and of the *para*-enriched hydrogen (b) adsorbed on CsX zeolite with Si:Al = 1.4 at 77 K and 20 kPa.

seen that, for the *para*-enriched hydrogen, the high-frequency band at 4745 cm^{-1} is much weaker. In contrast, the intensity of the band at $4425\text{--}4465\text{ cm}^{-1}$ increases. Since the main difference between the IR spectra of *ortho*- and *para*-modifications is associated with rotational transitions, these data quite definitely prove that the first band belongs to the vibration-rotational transition of adsorbed *ortho*-hydrogen, while the latter is due to the similar transitions of *para*-hydrogen. Then, similar to oscillations of adsorbed hydrogen relative to adsorption sites, the frequencies of rotations of adsorbed molecules can also be obtained as a differences between the wavenumbers of corresponding vibration-rotational bands and those of stretching vibrations.

The simplest theory of the above DRIFT spectra could be worked out in the framework

of the Stark effect, i.e., for the model of hydrogen polarization inside the zeolite micropores by the electric field created by exchangeable cations. For example, the vibrational–rotational spectra of molecular hydrogen and deuterium induced in solid hydrogens (H_2 , HD, D_2 , HT, DT) by point charges produced by irradiation with protons or β -particles were rationalized in Ref. [13]. The application of this theory to hydrogen adsorbed on zeolites reveals that polarization by electric field can explain the appearance of H–H stretching bands and of the combination of stretching bands with rotational and translational motion (oscillation) of hydrogen relative to the adsorption sites. The Stark effect also results in a proper selection rule for rotational transitions with $\Delta J = +2$ and thus explains the individual vibration-rotational spectra for *ortho*- and *para*-hydrogen. In addition, it describes reasonably well relative intensities of the stretching and vibrational–rotational bands.

On the other hand, the simplest model of hydrogen polarization by point charges does not reproduce properly the positions of all experimentally observed IR bands. For instance, to explain the low-frequency shift of H–H stretching vibrations for dihydrogen adsorbed on CsX zeolite equal to 65 cm^{-1} , the electric field created by cesium cations should be as high as $1.5 \cdot 10^8\text{ V/cm}$. However, this is in a contradiction with the almost free rotation of adsorbed molecules which in such a high field should be strongly hindered. In contrast, the weaker fields resulting in almost free rotation of hydrogen could not explain the value of the low-frequency shift of stretching vibrations and the experimentally observed separations of satellites from the main stretching bands of $100\text{--}150\text{ cm}^{-1}$.

Thus, for a more adequate description of the experimentally observed DRIFT spectra a more realistic geometry of the adsorption sites should be considered instead of the simplest model of hydrogen adsorption on the point charges or, in addition to the purely electrostatic interaction, some other factors contributing to the adsorption bond should be taken into account.

2.2. The nature of adsorption sites

It was earlier suggested in Refs. [3–5] that, due to the sign of the quadrupole moment, molecular hydrogen adsorbs on zeolites on exchangeable alkaline cations resulting in formation of ‘T-shape’ adsorption complexes. In this connection, let us summarise the modern data on sodium distribution in supercages of X and Y faujasites.

According to the recent very precise X-ray single crystal study by Olson [14], sodium ions occupy in supercages of NaX zeolite with Si:Al = 1.18 almost all available S_{II} sites (31.0 ions per the unit cell with 97% of the occupation) and 62% of the available S_{III} sites (29.8 ions per the supercage). It is also quite clear that, for X zeolites with lower Si:Al ratios, the population of S_{III} sites by sodium should increase and approach 100%. As a result for the zeolite with Si:Al = 1 the most homogeneous distribution of exchangeable cations can be attained. Therefore, according to the X-ray data, for NaX zeolites, one should expect hydrogen adsorption on sodium ions both at S_{II} and S_{III} sites.

In contrast, for NaY zeolites, the XRD [15] and inelastic neutron scattering data [16] indicate that sodium ions occupy only S_{II} sites (ca. 30 S_{II} sites per the supercage with the occupation factor of ca. 95%), while S_{III} sites remain free. Therefore, for this zeolite, only one kind of adsorption sites represented by sodium cations at S_{II} sites should be considered, while the number of adsorbed hydrogen molecules should be essentially less than for X zeolites.

This is in reasonable agreement with our experimental results on hydrogen adsorption on sodium forms of faujasites with different silica to aluminum ratios in the framework. Indeed, the total number of hydrogen molecules adsorbed on NaY zeolite is about twice less than that on NaX zeolites, while for NaY, the shape of adsorption isotherms indicates weaker hydrogen adsorption on sodium ions at S_{II} sites in comparison with adsorption on NaX (Fig. 4). Moreover, the adsorption isotherm for NaX can

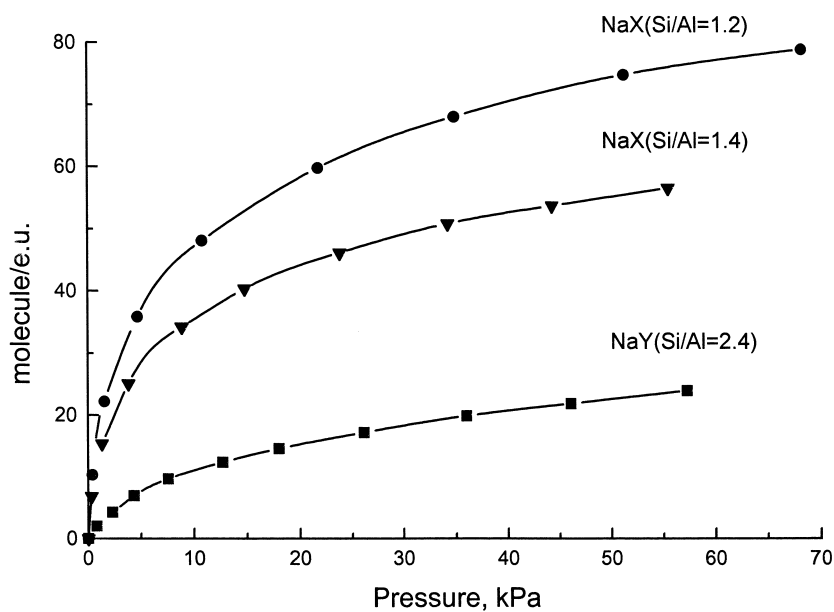


Fig. 4. Adsorption isotherms of hydrogen at 77 K on faujasites with different Si:Al ratio in the framework. The amount of adsorbed hydrogen is expressed in molecules per one unit cell of the zeolite.

be deconvoluted into two isotherms: one for weakly adsorbed hydrogen on sodium ions at S_{II} sites and another one for the stronger adsorption of hydrogen on sodium at S_{III} sites.

The adsorption data for NaX zeolite generally agree with DRIFT spectra which also quite clearly indicate the presence of two different adsorption sites (Fig. 5 and Table 1). The

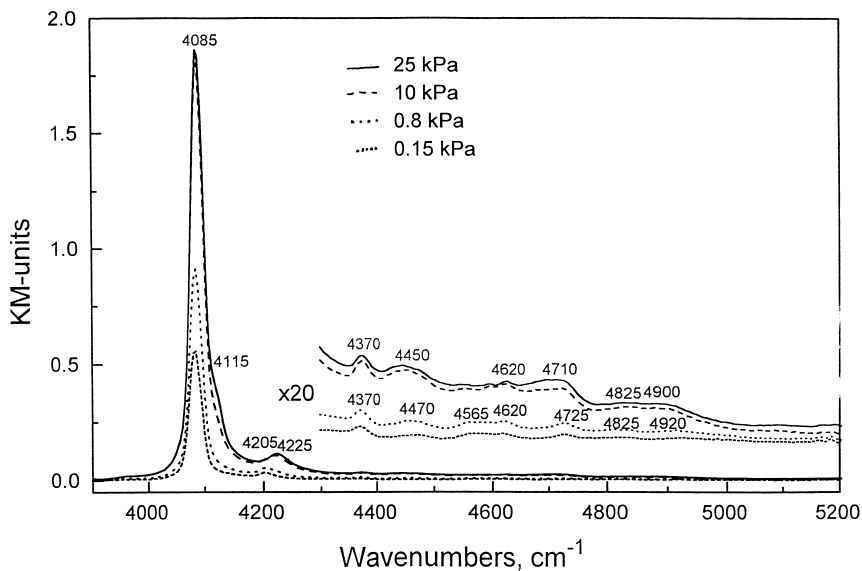


Fig. 5. DRIFT spectra of dihydrogen adsorbed at different pressures on NaX zeolite with Si:Al = 1.4 at 77 K.

stronger sites are related to H–H stretching band with the maximum at 4085 cm^{-1} . These sites are saturated with adsorbed hydrogen at a pressure of about 10 kPa, while the comparison of DRIFT spectra with the adsorption isotherm indicates that this pressure corresponds to adsorption of about one half of hydrogen on S_{III} sites.

The more careful study of the shape of the main stretching bands of hydrogen adsorbed at NaX zeolites with different Si:Al ratios in the framework at a low pressure reveals inhomogeneity of S_{III} adsorption sites which was also detected earlier by XRD in Ref. [14]. This results in the appearance of additional shoulders of the H–H stretching band at lower and higher wavenumbers and in the shift of the maximum of this band from 4082 to 4090 cm^{-1} at higher Si:Al ratios (Fig. 6).

Adsorption of hydrogen at higher pressures occurs on the weaker S_{II} sites in parallel with an appearance of the shoulder of the stretching band at 4115 cm^{-1} which, therefore, corresponds to the weaker form of hydrogen adsorption (Fig. 5). However, due to the different extinction coefficients one cannot compare the intensity of this shoulder with that of the main line at $4080\text{--}4090\text{ cm}^{-1}$.

In contrast to NaX, the results obtained by DRIFT spectroscopy for hydrogen adsorption on NaY are quite unexpected. Indeed, as was already mentioned above, according both to XRD and to inelastic neutron scattering data [15,16], sodium cations occupy in supercages of this zeolite only S_{II} sites, while S_{III} sites remain free. In other words, only one kind of adsorption centres should be expected. However, the DRIFT spectra of adsorbed hydrogen clearly indicate three different adsorption sites which correspond to two well-resolved H–H stretching bands with maxima at 4095 and 4115 cm^{-1} and a high-frequency shoulder at 4140 cm^{-1} at higher pressure (Fig. 7). This also agrees with results by Jelinek et al. [17] who also observed inhomogeneity of sodium ions at S_{II} sites in NaY zeolite by MAS NMR.

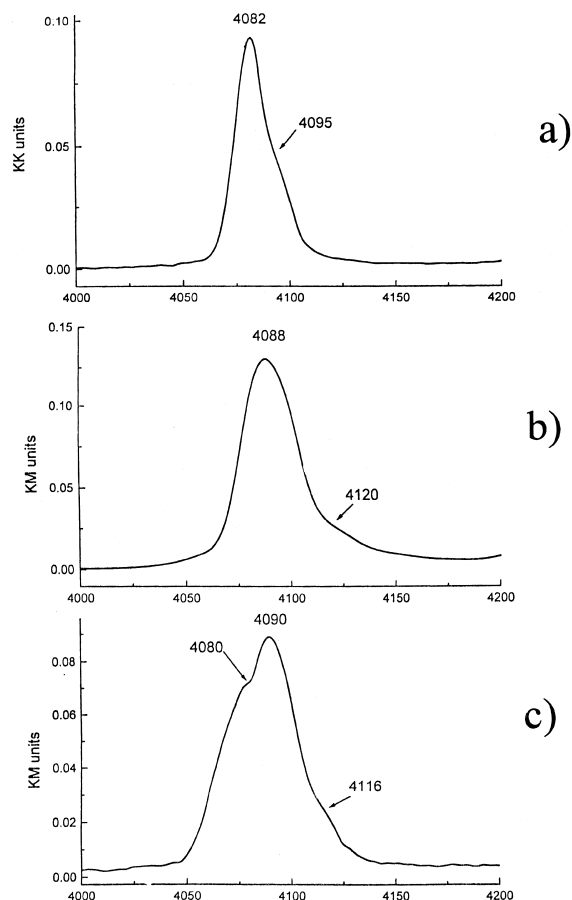


Fig. 6. The shape of the main H–H stretching band in DRIFT spectra of hydrogen adsorbed at 77 K at low pressure of 0.15 kPa on NaX zeolites with different Si:Al ratios in the framework. (a) Si:Al = 1.05; (b) Si:Al = 1.2; (c) Si:Al = 1.4.

In our belief, such a difference between X-ray and inelastic neutron scattering data, on the one hand, and DRIFT spectra of adsorbed hydrogen on the other, can be quite naturally explained by the influence on the hydrogen adsorption of aluminum distribution in the framework of faujasites. Indeed, the numerous ^{29}Si MAS NMR data clearly indicate that a random distribution of aluminum atoms in the framework of these materials results in different local Si:Al ratios [18]. In a similar way, the local distribution of Al atoms at S_{II} sites can also be different. According to Lowenstein rule [19], these sites can contain in NaY zeolites one, two or three aluminum atoms in the six-membered rings cor-

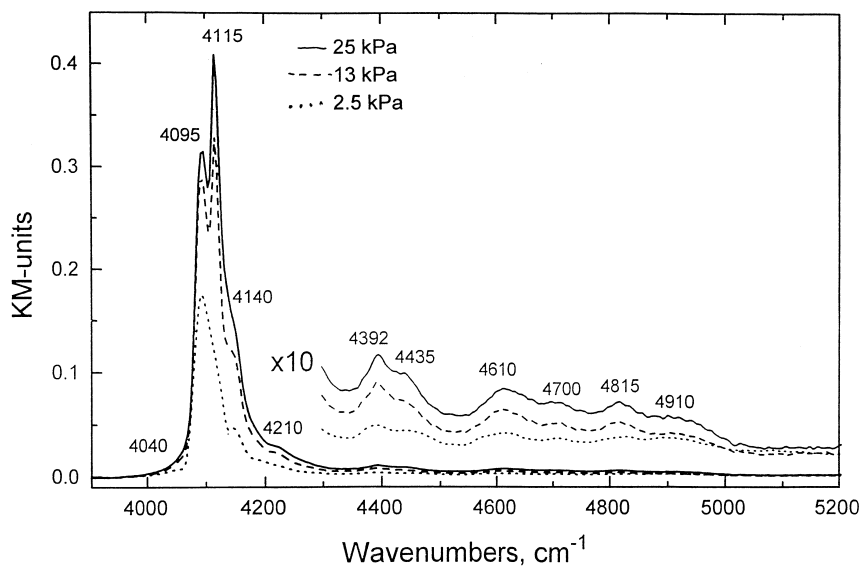


Fig. 7. DRIFT spectra of dihydrogen adsorbed at different pressures on NaY zeolite with Si:Al = 2.4 at 77 K.

responding to three different sites of hydrogen adsorption depicted in Fig. 8. In other words, the inhomogeneity of adsorption sites indicates that adsorption of hydrogen merely on cations is rather unlikely. Instead the adsorption sites are represented both by alkaline cations and by the neighbouring basic oxygen atoms of the zeolite framework as was earlier suggested by us in Refs. [20,21].

The results of this paper present the further arguments in favour of this conclusion. Indeed, the important role of basic oxygen of the zeolite framework is also supported by the higher frequencies of adsorbed hydrogen oscillations relative to adsorption sites for the more basic NaX

zeolite in comparison with NaY zeolite and by the larger low-frequency shifts of H–H stretching vibrations resulting from adsorption.

Thus, the DRIFT study of low-temperature hydrogen adsorption is a very sensitive tool for analysis of the distribution of exchangeable cations and of aluminum atoms in the zeolite frameworks.

3. Vibrations and hindered rotation of adsorbed hydrogen

Unlike the above simplest case of dihydrogen adsorption on CsX zeolite, the vibration-rotation-

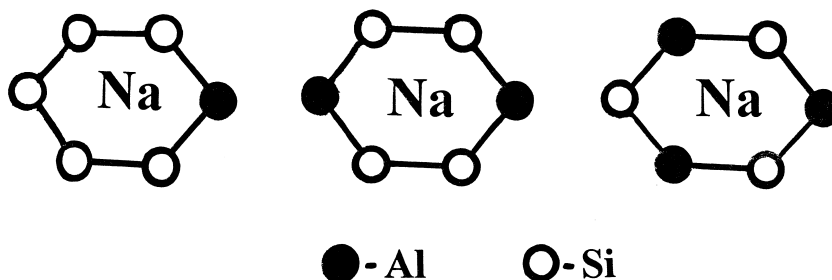


Fig. 8. S_{II} adsorption sites with different local distribution of aluminum atoms in the six-membered rings.

tional structure of DRIFT spectra of hydrogen adsorbed on sodium and alkaline earth forms of X and Y zeolites is more complicated. The most well resolved spectra were obtained in our experiments with hydrogen adsorbed on BaX zeolite. They are presented in Fig. 9a and b (see also Table 1).

It follows from these data that, for adsorption of *para*-enriched hydrogen, the high-frequency bands at 4420, 4610, 4810 and at 4950 cm^{-1} are extremely weak. In contrast, the intensity of the bands at 4270, 4375 and at 4600 cm^{-1} increases. Similar to the above spectrum of hydrogen adsorbed on CsX, these data quite definitely prove that the first three bands belong to the vibration-rotational transitions of adsorbed *ortho*-hydrogen, while the four latter bands are due to vibration-rotational transitions of *para*-hydrogen.

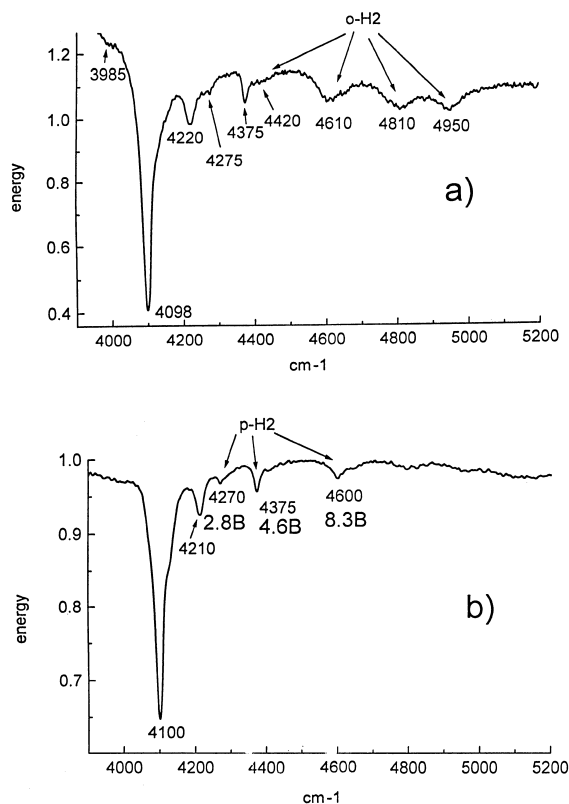


Fig. 9. DRIFT spectra of conventional hydrogen with *ortho:para* ratio equal to 3 (a) and of the *para*-enriched hydrogen (b) adsorbed on BaX zeolite at 77 K at 20 kPa.

The more complex vibration-rotational structure indicates that rotation of hydrogen is partially hindered. Indeed, according to the above-discussed simplest Stark effect approach, to the crystal field theory [22], and to quantum chemical calculations [23–25], the hindered rotation removes the degeneracy of rotational levels and results in splitting of vibration-rotational bands. For instance, for the partially hindered rotation of hydrogen in a cubic force field, the vibration-rotational bands of *para*-hydrogen and *ortho*-hydrogen should split into doublet and triplet, respectively [23]. For the out-of-plane hindered rotation, the vibration-rotational spectrum is even more complex. For *para*-hydrogen the spectrum should contain three vibration-rotational bands, whereas for *ortho*-modification it should consist of four bands [25]. This exactly corresponds to hydrogen adsorption on BaX, while the splittings of the vibration-rotational bands allow one to estimate the height of the hindering barrier of about 10 B or ca. 600 cm^{-1} .

In a similar way, the spectra of conventional hydrogen with *ortho*- to *para*-ratio equal to 3 and of the *para*-enriched hydrogen adsorbed on LiX zeolite also indicate a partially hindered rotation (Fig. 10). Thus, DRIFT spectra provide a quite unique information concerning rotation of adsorbed molecules, which could not be obtained by any other technique.

At the first glance, these results on hindered rotation of hydrogen could be quite naturally explained by a somewhat stronger interaction of adsorbed molecules with more positively charged Ba^{2+} cations or with smaller Li^{+} cations with the radius of only 0.68 Å in comparison with bigger Cs^{+} cations with the ion radius of 1.67 Å. However, the difference in hydrogen adsorption strength is hardly seen from the virtually equal shapes of adsorption isotherms for different alkaline forms of X zeolite depicted in Fig. 11. (To make possible the comparison of the results for different cationic forms, we expressed the amounts of adsorbed hydrogen as the numbers of hydrogen molecules

adsorbed by one alkaline cation in the framework.) Moreover, the slightly lower hydrogen adsorption on LiX is not consistent with the above-mentioned smallest radius of Li^+ cation, with the smallest low-frequency shift of stretching vibrations of adsorbed hydrogen, and with the smallest separation of the high-frequency satellite from the main stretching band which also indicates a weaker interaction of adsorbed hydrogen with Li^+ cations (Table 1).

However, one has to discriminate the desorption heat and the motion of adsorbed molecules relative to adsorption sites. Indeed, desorption results in complete dissociation of the adsorption bond, whereas the hindered rotation or oscillation of adsorbed hydrogen relative to the adsorption sites remain this bond nondissociated. Therefore, the rotations and vibrations of adsorbed molecules are mainly related to the

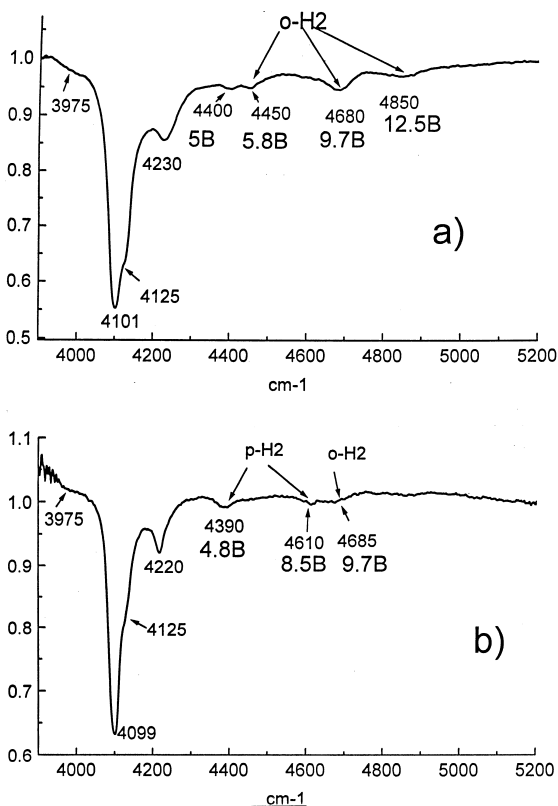


Fig. 10. DRIFT spectra of conventional hydrogen with *ortho*:*para* ratio equal to 3 (a) and of the *para*-enriched hydrogen (b) adsorbed on LiX zeolite at 77 K at 20 kPa.

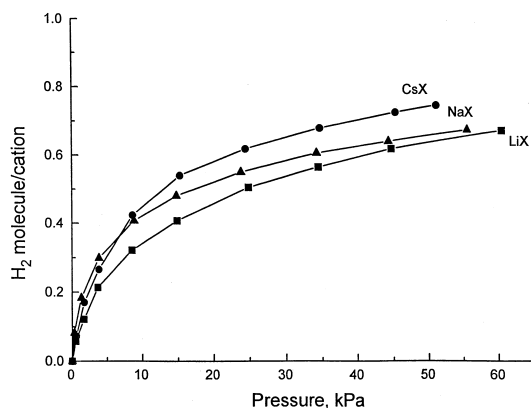


Fig. 11. Adsorption isotherms of hydrogen on different alkaline-metal forms of NaX zeolite with Si:Al = 1.4 at 77 K.

shape of potential at the bottom of the potential well, while adsorption heat is associated with the entire depths of the well which depends both on interaction of hydrogen with cations and surrounding basic oxygen atoms on the walls of the zeolite cavities. In other words, the hindered rotation and oscillations of adsorbed molecules is more strongly dependent on the local interaction of hydrogen with cations, while the adsorption heat is linked with interaction with cations and surrounding basic oxygen of the zeolite framework. Therefore, the wavenumbers of satellites and those of hindered rotation should be rather related to diffusion of adsorbed molecules from one adsorption site to another than with the adsorption heat.

4. Relation between DRIFT spectra and diffusion of hydrogen inside the zeolite micropores

The above conclusions concerning the motion of adsorbed hydrogen molecules relative to adsorption sites make possible to compare DRIFT spectra with diffusion of hydrogen inside the micropores of zeolites. Indeed, according to results obtained by the field gradient NMR [26], the diffusion coefficient D of hydrogen in NaX zeolite changes in the temperature interval 110–150 K from 0.5×10^{-8} to $3 \times$

10^{-8} m²/s with an activation energy of about 5 kJ/mol. From these data, the lifetime τ of hydrogen inside the supercages of the zeolite may be estimated from the following well known expression for the random walk [27], i.e., $\tau = l^2/2D$. For $l = 1.3 \times 10^{-9}$ m (ride supra) and $T = 110$ K, this results in $\tau \approx 2 \times 10^{-10}$ s.

It also follows from Ref. [26], that the activation energy of hydrogen diffusion in the narrow pore NaA zeolite is lower than that in the large pore NaX. Obviously, this implies that diffusion of hydrogen in NaX zeolite is not limited by penetration through the twelve-membered windows which connect the adjacent supercages of the zeolite framework, but is rather determined by the successive adsorption on several sodium cations inside the supercages. Therefore, the activation energy of diffusion, reported in Ref. [26] represents the energy barrier for jumping of H₂ molecules from one adsorption site to another *inside* the large cavities. Then, the residence time of hydrogen adsorbed by each sodium cation, τ^* can be estimated from the frequency ω_0 of hydrogen oscillations relative to adsorption sites obtained from DRIFT spectra and the activation energy of diffusion.

Indeed, for NaX, the difference between wavenumber of the high-frequency satellite and the main stretching band corresponds to $\omega_0 = 4.2 \times 10^{12}$ s⁻¹ (see also Table 1). Then, at 110 K, the life time of an H₂ molecule at sodium adsorption sites inside the large cavities τ^* is equal to about 6×10^{-11} s. This means that the residence time of hydrogen inside the supercages at 110 K is about one order of magnitude longer than that at each sodium cation. Thus, prior to migration to the adjacent cavity, the hydrogen molecule is about ten times successively adsorbed by different sodium ions at S_{II} or S_{III} sites.

On the other hand, the activation energy of diffusion, $E_{\text{diff}} = 5$ kJ/mol corresponds to the wavenumber of 418 cm⁻¹. This is three times greater than the separation of the high-frequency satellite from the main stretching band and corresponds to the excitation of the adsorption

bond of the hydrogen molecule to the third vibrational level (viz. $3 \times 140 = 420$ cm⁻¹). Thus, DRIFT spectra and NMR data represent a self consistent model for adsorption and diffusion of hydrogen molecules inside the micropores of faujasites.

5. Conclusion

The sites of hydrogen adsorption in alkaline–metal forms of zeolites are most likely represented by alkaline cations and the adjacent basic oxygen atoms of the framework. The important role of basic oxygen of the zeolite framework follows from adsorption isotherms, from the frequencies of oscillation of adsorbed hydrogen molecules relative to the adsorption sites and from the low-frequency shifts of H–H stretching vibrations resulting from adsorption. The strength of hydrogen adsorption on such sites depends on their geometry. It is stronger on S_{III} sites where sodium ions are surrounded by four adjacent oxygen atoms than on S_{II} sites where the number of the closest oxygen atoms is equal to six.

For NaY zeolites, the perturbation of H–H stretching vibrations by such acid–base pairs can be also used to monitor the smaller differences between sodium atoms at S_{II} sites resulting from the local distribution of aluminum atoms in the six-membered rings of the framework. Such information is quite unique and demonstrates a high sensitivity of the low temperature hydrogen adsorption with a DRIFT control of H–H stretching frequency perturbation as a molecular probe for the study of zeolites.

The DRIFT bands of a combination of H–H stretching vibrations with rotation of adsorbed molecules are more sensitive to the nature of the exchangeable cations. This results in almost free rotation of hydrogen molecules adsorbed by the largest Cs⁺ cations and in strongly hindered rotation for hydrogen adsorption on the smallest Li⁺ or on the bivalent Ba²⁺ cations.

Finally, the separations from the main stretching bands of satellites allows one to estimate the frequency of vibration of adsorbed hydrogen molecules relative to adsorption sites and the residence time of adsorbed molecules at sodium cations. The latter value indicates that diffusion of hydrogen in faujasites is limited by jumping of adsorbed molecules from one alkaline–metal cation to another inside the zeolites supercages.

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References

- [1] D.W. Breck, *Zeolite Molecular Sieves*, Wiley, London, 1974.
- [2] H. Förster, M. Schuldt, *J. Chem. Phys.* 66 (1977) 5237.
- [3] H. Förster, M. Schuldt, *J. Mol. Struct.* 61 (1980) 361.
- [4] H. Förster, W. Freude, G. Peters, in: H.G. Karge, J. Weitkamp (Eds.), *Zeolites as Catalysts, Sorbents and Detergent Builders*, Elsevier, Amsterdam, 1989, pp. 545–554.
- [5] H. Förster, in: J.E.D. Davies (Ed.), *Spectroscopic and Computational Studies of Supramolecular Systems*, Kluwer Acad. Pub., Amsterdam, 1992.
- [6] V.B. Kazansky, V.Yu. Borovkov, L.M. Kustov, *Proc. 6th Int. Congr. on Catalysis*, Vol. 3, Dachema Verlag Chemie, Berlin, 1984, p. 3.
- [7] L.M. Kustov, V.B. Kazansky, *J. Chem. Soc., Faraday Trans.* 87 (1991) 2675.
- [8] V.B. Kazansky, in: G. Öhlmann, H. Pfeifer (Eds.), *Catalysis and Adsorption by Zeolites*, Elsevier, Amsterdam, 1991, pp. 117–131.
- [9] A.Yu. Khodakov, L.M. Kustov, V.B. Kazansky, C. Williams, *J. Chem. Soc., Faraday Trans.* 88 (1992) 3251.
- [10] K. Beck, H. Pfeifer, S. Staudte, *J. Chem. Soc., Faraday Trans.* 89 (1993) 3995.
- [11] V.B. Kazansky, V.Yu. Borovkov, H.G. Karge, *J. Chem. Soc., Faraday Trans.* 93 (1997) 1843.
- [12] V.B. Kazansky, V.Yu. Borovkov, H.G. Karge, *J. Chem. Soc., Faraday Trans.*, 1997 (submitted).
- [13] J.D. Poll, J.L. Hunt, *Can. J. Phys.* 63 (1985) 84.
- [14] D.H. Olson, *Zeolites* 15 (1995) 439.
- [15] G.R. Eulenberger, D.P. Shoemaker, J.G. Keil, *J. Phys. Chem.* 72 (1968) 4366.
- [16] V. Bosacek, S. Beran, Z. Ilrak, *J. Phys. Chem.* 65 (1981) 3859.
- [17] R. Jelinek, S. Oskar, G.A. Ozin, *J. Am. Chem. Soc.* 114 (1992) 4907.
- [18] G. Engelhardt, U. Lohse, V. Patzelova, M. Magi, E. Lipmaa, *Zeolites* 3 (1983) 329.
- [19] W. Loewenstein, *Am. Mineralog.* 39 (1954) 95.
- [20] E. Garrone, V.B. Kazansky, L.M. Kustov, J. Sauer, I.N. Senchenya, P. Uglengo, *J. Phys. Chem.* 96 (1992) 1040.
- [21] V.B. Kazansky, in: J. Fraissard, L. Petrakis (Eds.), *Acidity and Basicity of Solids*, Vol. 444, NATO ASI Series, 1994, pp. 353–374.
- [22] R.E. Miller, J.C. Decuis, *J. Chem. Phys.* 59 (1973) 4871.
- [23] A.F. Devonshire, *Proc. R. Soc.* 153A (1936) 601.
- [24] H.M. Cundy, *Proc. R. Soc.* 164A (1938) 420.
- [25] T.B. MacRury, J.R. Sams, *Mol. Phys.* 19 (1970) 337.
- [26] N.K. Bär, J. Kärger, 9 *Deutsche Zeolite Tagung*, 3–5 März 1997, p. 59.
- [27] J. Kärger, D.M. Ruthven, *Diffusion in Zeolites and other Microporous Solids*, Wiley, New York, 1992, p. 24.