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Diffuse-Reflectance IR Spectra of *ortho*-Hydrogen and *para*-Hydrogen Adsorbed on Zeolite BaX at 77 K and Their Interpretation in Terms of the Stark Effect

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Abstract—The vibrational and vibrational–rotational spectra of hydrogen adsorbed on zeolite BaX at 77 K were examined by diffuse-reflectance IR spectroscopy over a wide range of wavenumbers. The use of hydrogen enriched in the para isomer and of molecular deuterium allowed us to reliably assign the absorption bands to orthohydrogen and *para*-hydrogen and compare the experimentally observed band splitting with the theoretically calculated shifts of the corresponding levels resulted from the Stark effect. In the calculations, an adsorption site was simulated as a positive point charge. Although this approximation is rough, the IR spectra of adsorbed hydrogen and deuterium are adequately described in terms of the Stark effect. A decrease in the frequency of stretching vibrations of H–H (D–D) bonds in the molecules coordinated to Ba^{2+} cations, a decrease in the intensity of vibrational–rotational absorption bands, and the band splitting in the spectra of adsorbed *para*-hydrogen and orthohydrogen were explained.

INTRODUCTION

It is well known that zeolites containing bivalent alkaline-earth metal cations exhibit catalytic activity in hydrocarbon reactions, and the smaller the radius of exchanged cations, the higher this activity [1, 2]. It is believed that this is due to the effect of strong electrostatic fields generated by exchanged cations in the cavities of zeolites. These fields can induce a shift in the energy levels of valence electrons in adsorbed molecules and hence significantly affect adsorption and catalysis processes in zeolites [2]. Probe molecules whose IR spectra are sensitive to the strength and configuration of these fields can be used for the spectroscopic examination of electrostatic fields in zeolite cavities. In particular, adsorbed molecular hydrogen can serve as a probe, the IR spectra of which can be observed only in the case of molecule polarization.

The transmission and diffuse-reflectance IR spectra of molecular hydrogen adsorbed on zeolites A, X, and Y containing univalent alkali metal cations at a boiling temperature of nitrogen were studied previously [3–8]. The appearance of intense fundamental bands of stretching vibrations of the H–H bonds was explained by polarization of hydrogen molecules due to the adsorption of cations or acid–base pairs formed by a cation and the neighboring oxygen atom of the zeolite framework. A decrease in the frequency of stretching vibrations of adsorbed hydrogen, which was as high as 80 cm^{-1}, was also explained by polarization of the H–H bond.

With the use of alkaline forms of faujasites as an example, it was also found [5] that in addition to the fundamental bands of stretching vibrations and satellite bands that resulted from a combination of stretching vibrations of adsorbed hydrogen and vibrations of the molecule as a whole relative to adsorption sites, low-intense high-frequency bands were present in the diffuse-reflectance IR spectra. These bands were assigned to the vibrational–rotational transitions of orthohydrogen and *para*-hydrogen. As judged from the splitting of absorption bands, the rotation of adsorbed molecules is partially hindered [5, 8].

In this work, we attempted to quantitatively evaluate the electrostatic field strength in the cavities of zeolite BaX from the IR spectra of adsorbed hydrogen on the basis of the Stark effect. As estimated in [9], the electrostatic field strength nearby exchanged cations can be as high as 10^8 V/cm. This field will induce a considerable oscillating dipole moment in a rotating adsorbed H_2 molecule, which exhibits anisotropic polarizability. As a result of this, dipole vibrational–rotational transitions with a change in the rotational quantum number J to or ± 2 can occur under the action of electromagnetic radiation [10].

Low-frequency shifts of the absorption bands of stretching vibrations of H–H bonds in adsorbed molecules by more than 100 cm^{-1} can also be explained by the Stark effect [11]. In particular, these shifts of the absorption bands of stretching vibrations of D–D and H–D bonds were observed in the IR spectra of solid D_2 and HD upon the generation of positively charged defects by irradiation with a proton beam of 15-MeV [12, 13].

We chose the barium form of zeolite X because bivalent barium cations, in contrast to univalent alkali metal cations, are localized in the large cavities of fau-

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jasites, primarily, at S_{II} sites [9], and they are more uniform sites for hydrogen adsorption than univalent cations. In this case, the IR spectra of adsorbates exhibit comparatively narrow well-resolved absorption bands in the region of vibrational–rotational transitions. This fact allowed us to more reliably assign the bands to orthohydrogen and *para*-hydrogen and compare the experimental splitting of the bands with the theoretically calculated shifts of the corresponding energy levels due to the Stark effect.

EXPERIMENTAL

Zeolite X (Si/Al = 1.4) with an approximately 80% degree of exchange of Na^+ ions for Ba^{2+} was used in this study. Samples were placed in quartz cells and pretreated in a vacuum at 673 K for 4 h. After the pretreatment, the zeolites were cooled to 77 K, and hydrogen or deuterium was adsorbed on them at various equilibrium pressures.

The diffuse-reflectance IR spectra of adsorbed hydrogen (deuterium) were measured using a 2000 FT Perkin-Elmer Fourier IR spectrophotometer in the quartz cells used for the pretreatment of zeolites. The instrument was equipped with a homemade diffuse-reflectance attachment, which was described elsewhere [5]. Gas-phase hydrogen (deuterium) was not evacuated in the course of measurements because it gave no additional absorption bands in the IR spectra. A quartz Dewar flask filled with liquid nitrogen was used to maintain a constant temperature of 77 K in the course of recording the spectra. The diffuse-reflectance spectra were converted into Kubelka–Munk units, taking the reflection factor of zeolites to be equal to 0.9 at a frequency of 5000 cm^{-1}.

Hydrogen enriched in the para isomer was obtained according to the procedure described in [14]. For this purpose, an equilibrium mixture (at room temperature) of *para*- and *ortho*-H_2 was adsorbed on activated carbon, which is an active catalyst of the *ortho–para* conversion, at a boiling temperature of liquid helium. Next, hydrogen enriched in the para isomer desorbed from the carbon at ~20 K. According to our estimates, the para isomer content in desorbed hydrogen was 70–80%.

RESULTS AND DISCUSSION

Figure 1 demonstrates the spectra of H_2 adsorbed on zeolite BaX at 77 K and different equilibrium pressures. The intense absorption bands at 4100 cm^{-1} are due to the stretching vibrations of H–H bonds in molecules that interact with Ba^{2+} cations. As in the case of hydrogen adsorption on zeolites containing univalent cations, in addition to these absorption bands, the spectra also exhibit low-intense high-frequency bands. These bands can be assigned to the Raman modes of H–H stretches and vibrations of the whole molecules relative to adsorption sites and to the vibrational–rotational transitions of *ortho*-hydrogen and *para*-hydrogen. It can be seen in Fig. 1 that the intensities of all of the above absorption bands monotonically decreased with a decrease in the hydrogen pressure. In this case, the ratio between the intensities of the bands corresponding to H–H stretching vibrations, Raman modes, and vibrational–rotational transitions remained almost unchanged. Hence, it follows that all these absorption

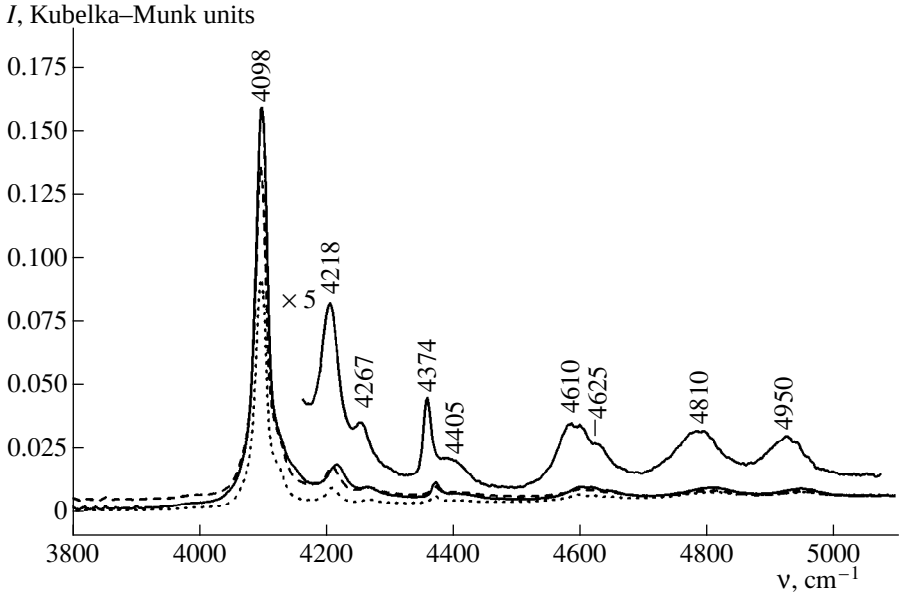

Fig. 1. IR spectra of hydrogen adsorbed on zeolite BaX at 77 K and equilibrium pressures of 100 (solid line), 15 (dashed line), and 1 torr (dotted line).

bands are assigned to one type of complexes of H_2 molecules with Ba^{2+} cations, in which the H_2 molecules exhibit complicate motions including rotation and low-frequency vibration relative to adsorption sites.

Figure 2 shows a spectrum of hydrogen enriched in the para isomer adsorbed on zeolite BaX at 77 K at an equilibrium pressure of 100 torr. The adsorption bands at 4420, 4625, 4810, and 4950 cm^{-1} are virtually absent from this spectrum. Thus, they should be attributed to the absorption bands of the vibrational–rotational structure of *ortho*-hydrogen. The absorption bands at 4373–4374 and 4600–4610 cm^{-1}, which are present in the spectra of both an adsorbed equilibrium mixture (Fig. 1) and hydrogen enriched in the para isomer (Fig. 2), correspond to the vibrational–rotational structure of *para*-hydrogen. As in the case of analogous bands of hydrogen adsorbed on zeolite NaA [5], the assignment of the other two absorption bands at 4212–4218 and 4267–4270 cm^{-1} can be performed by a comparison between the spectra of adsorbed hydrogen (Figs. 1, 2) and deuterium (Fig. 3).

The absorption bands at 4212–4218 and 3035 cm^{-1} were assigned to the Raman modes of H–H and D–D stretches and vibrations of the whole H_2 and D_2 molecules relative to adsorption sites, respectively. This assignment is based on isotopic shifts that appear on the replacement of hydrogen by deuterium. Indeed, the vibration frequencies of H_2 and D_2 molecules relative to adsorption sites, calculated as the frequency differences between Raman modes and H–H and D–D stretching vibrations in the H_2–Ba^{2+} and D_2–Ba^{2+} complexes, are ~115 and 86 cm^{-1}, respectively. The ratio between these frequencies is ~1.34. As would be expected for the harmonic vibrations of H_2 and D_2 molecules about adsorption sites, this value is close to the ratio between the masses of deuterium and hydrogen molecules to the 1/2 power. The assignment of the absorption bands with maxima at 4267–4270 and 3088 cm^{-1} is ambiguous. They may be attributed to the vibrational–rotational transitions of *para*-hydrogen and orthodeuterium, because the ratio between the vibration frequencies of the corresponding low-frequency modes is 1.9; i.e., it is close to the ratio between the molecular masses of D_2 and H_2. Moreover, the absorption band with a maximum at 4270 cm^{-1} is present in the spectrum of adsorbed hydrogen enriched in the para isomer (see Fig. 2). On the other hand, this absorption band can also be attributed to the combination mode of stretching vibrations of the H–H bond and to the first overtone of vibrations of the whole H_2 molecule relative to the adsorption site. The almost equal intensity ratios of the absorption bands at 4212–4218 and 4267–4270 cm^{-1} in the spectra of the adsorbed equilibrium mixture of *ortho*-hydrogen and *para*-hydrogen (Fig. 1) and that of hydrogen enriched in the para isomer (Fig. 2) support this assignment.

Let us analyze this situation by simulating the vibrations of H_2 and D_2 molecules about adsorption sites as linear anharmonic oscillators. The potential energy of this oscillator has the form of the Morse function

$$U(r) = -2De^{-ar} + De^{-2ar}, \quad (1)$$

where D is the dissociation energy of the Ba–H_2 or Ba–D_2 bond, r is the shift of the center of gravity of the mole-

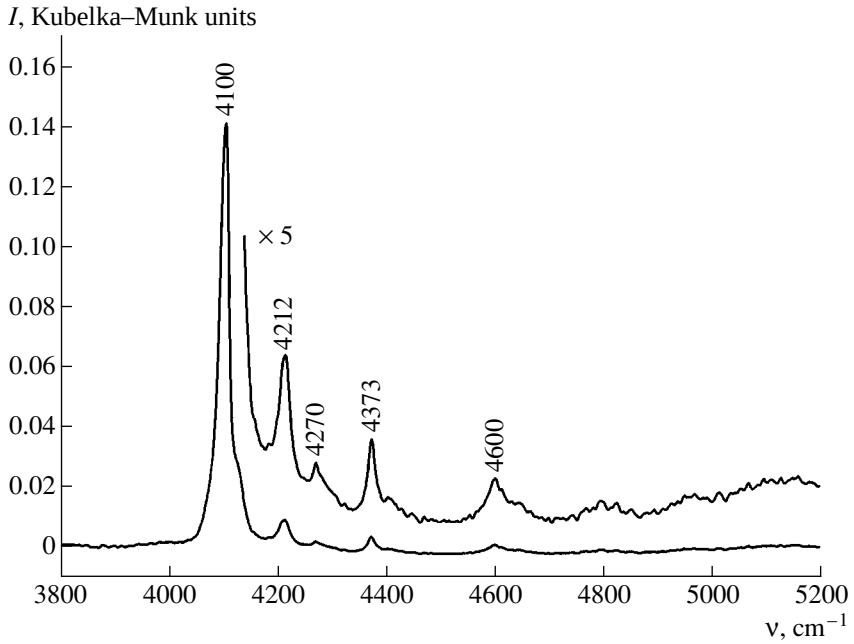

Fig. 2. IR spectrum of hydrogen, enriched in the para isomer, adsorbed on zeolite BaX at 77 K and an equilibrium pressure of 100 torr.

cule from the equilibrium position, and a is an empirical constant. In this case, the energy levels of molecular vibrations relative to adsorption sites have the form [15]

$$E = \left(n + \frac{1}{2}\right)h\nu - \frac{(h\nu)^2}{4D}\left(n + \frac{1}{2}\right)^2, \qquad (2)$$

where ν is the frequency of harmonic vibrations, and n is the vibrational quantum number.

The solution to Eq. (2) using the fundamental vibration and first overtone frequencies for adsorbed molecules of H_2 (115 and 168 cm^{-1}) and D_2 (86 and 139 cm^{-1}) calculated from the difference between the frequencies of the band maxima of combination tones and fundamental H–H and D–D vibrations resulted in the harmonic vibration frequencies $\nu(H_2)$ = 177 cm^{-1} and $\nu(D_2)$ = 119 cm^{-1}. The ratio between these frequencies is equal to 1.49, which is close to the ratio between the molecular masses of deuterium and hydrogen to the 1/2 power. The bond dissociation energies (D) calculated for the Ba–H_2 and Ba–D_2 complexes are 0.73 and 0.62 kcal/mol, respectively. The difference between these values of ~0.1 kcal/mol can result from inaccurate determination of the overtones and the frequencies of the fundamental molecular vibrations relative to adsorption sites. This determination was performed on the assumption that the vibration frequencies of combination tones agree with the sum of the frequencies of stretching vibrations of high-frequency and low-frequency modes.

Table 1 summarizes the positions and assignment of absorption band maxima in the spectra of hydrogen and deuterium adsorbed on zeolite BaX.

Now, we consider the vibrational–rotational structure of the spectra. It is well known [9] that Ba^{2+} cations in large cavities of zeolite X are localized at S_{II} sites, i.e., near the centers of six-membered windows. Let us assume that the electrostatic field produced by the cation and its nearest environment is aligned with the axis of symmetry of the adsorption site Z. In the case of weak electrostatic fields when H_2 molecules can almost freely rotate, the probability of the electric dipole vibrational–rotational transition with changes in the rotational quantum number (J) and the Z component of the angular momentum (M) (the $J_1, M_1 \longrightarrow J_2, M_2$ transition with a change in the vibrational quantum number by unity) can be calculated by the equation [16]

$$P(J_1, M_1 \longrightarrow J_2, M_2) = K\left|\int Y^*_{J_1M_1}(\theta, \varphi)\frac{dD_E}{dr}Y_{J_2M_2}(\theta, \varphi)d\Omega\right|^2, \qquad (3)$$

where $Y_{JM}(\theta, \varphi)$ is the spherical function that corresponds to the rotational quantum number J and the Z component of the angular momentum (M) of the molecule on the fixed coordinate system XYZ with the origin at the center of gravity of the molecule; θ is the angle between the molecular axis and the Z axis; φ is the angle between the XZ plane and the plane going through the Z axis and the molecular axis; $\frac{dD_E}{dr}$ is the derivative of the projection of the vector operator of the molecular dipole moment (D_E) onto the direction of the electric field strength of the electromagnetic wave with respect to the internuclear distance in the molecule (r);

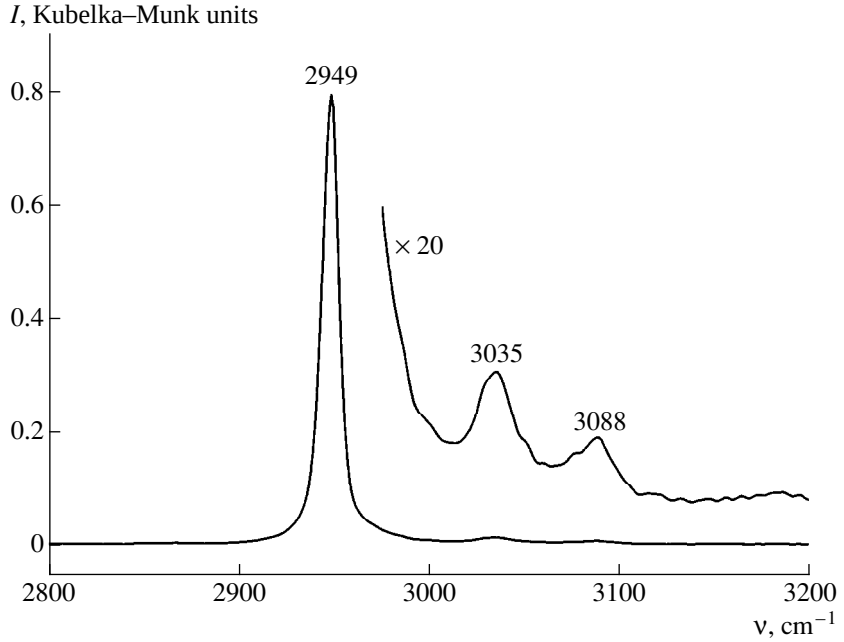

Fig. 3. IR spectrum of deuterium adsorbed on zeolite BaX at 77 K and an equilibrium pressure of 100 torr.

Table 1. Positions and assignment of absorption band maxima in the spectra of hydrogen and deuterium adsorbed on zeolite BaX

Adsorbate	*ortho*-H_2 + *para*-H_2	*ortho*-D_2 + *para*-D_2	*para*-H_2
H–H or D–D stretching vibrations	4098	2949	4100
H–H (D–D) stretching vibration + fundamental vibration and overtone of H_2 (D_2) vibrations about the adsorption site	4218, 4267	3035, 3088	4212, 4270
Vibrational–rotational transitions of *para*-H_2	4374, 4610	–	4373, 4610
Vibrational–rotational transitions of *ortho*-H_2	4405, 4625, 4810, 4950	–	–

$d\Omega$ is the solid-angle element that is the domain of integration; and K is a proportionality constant.

In the case of a polycrystalline sample and unpolarized light, this probability is

$$P(J_1, M_1 \longrightarrow J_2, M_2) = \frac{K}{3}\sum_{\beta}\left|\int Y^*_{J_1M_1}(\theta, \varphi)\frac{dD_\beta}{dr}Y_{J_2M_2}(\theta, \varphi)d\Omega\right|^2, \quad (4)$$

where D_β ($\beta = X, Y$, and Z) are the corresponding rectangular components of the dipole moment. These components can be expressed in terms of the components of the induced dipole moment, which correspond to the spherical functions $Y_{2\nu}$ ($\nu = 0, \pm1$) [11], as follows:

$$D_\nu = E\{\alpha\delta_{\nu0} + (1/3)\gamma(4-\nu^2)^{1/2}(4\pi/5)^{1/2}Y_{2\nu}(\theta, \varphi)\}, \quad (5)$$

namely,

$$D_Z = D_0, \quad D_X = D_{+1} + D_{-1}, \quad D_Y = -i(D_{+1} - D_{-1}), \quad (6)$$

where E is the electric field strength; $\alpha = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$ and $\gamma = \alpha_\parallel - \alpha_\perp$ are the average polarizability and the anisotropy of molecular polarizability, respectively; and $\delta_{\nu0}$ is the Kronecker symbol.

An analysis of expression (4) with consideration for (5) and (6) indicates that, when a dipole moment is induced in homonuclear diatomic molecules by an electrostatic field, the vibrational–rotational transitions with $\Delta J = J_1 - J_2 = 0, \pm2$ and $\Delta M = M_1 - M_2 = 0, \pm1$ are allowed.

Table 2 summarizes the relative intensities of vibrational and vibrational–rotational transitions allowed by selection rules for hydrogen and deuterium, as calculated by Eq. (3). The intensity of the $00 \longrightarrow 00$ vibrational transition for *para*-hydrogen and orthodeuterium was taken to be 100%. The required derivatives of the anisotropy of polarizability and of the average polarizability with respect to the distance to which nuclei shifted from an equilibrium position were evaluated from the calculated data on γ and α as functions of internuclear distance [17] as follows:

$$\frac{d\alpha}{dr} = 1.07 \text{ Å}^2, \quad \frac{d\gamma}{dr} = 0.84 \text{ Å}^2.$$

It follows from Table 2 that the total intensity of vibrational transitions (without changes in the quantum numbers J and M) is usually more than 50 times higher than the intensity of any vibrational–rotational transition. This is in complete agreement with our experimental data, according to which the absorption band intensities of vibrational–rotational transitions are of the order of 1% of the intensity of the fundamental band due to stretching vibrations of the H–H bonds in hydrogen adsorbed on zeolites.

To explain the low-frequency shift of the stretching vibrations of adsorbed H_2 and D_2 molecules, we use the calculated data [11] on the effect of the electrostatic field produced at the location of the center of gravity of molecules by a positive point charge on the vibra-

Table 2. Relative intensities of vibrational and vibrational–rotational transitions allowed by selection rules for hydrogen and deuterium

Isomer	Transition	Relative intensity of the transition, %
Para-hydrogen, orthodeuterium	$00 \longrightarrow 00$	100
	$00 \longrightarrow 20$	5.5
	$00 \longrightarrow 2 \pm 1$	8.3
Orthohydrogen, paradeuterium	$10 \longrightarrow 10$	146.3
	$1 \pm 1 \longrightarrow 1 \pm 1$	160.2
	$10 \longrightarrow 1 \pm 1$	4.8
	$1 \pm 1 \longrightarrow 10$	4.8
	$10 \longrightarrow 30$	4.2
	$10 \longrightarrow 3 \pm 1$	5.7
	$1 \pm 1 \longrightarrow 30$	2.2
	$1 \pm 1 \longrightarrow 3 \pm 1$	5.7
	$1 \pm 1 \longrightarrow 3 \pm 2$	7.0

tional–rotational levels. In this case, according to [11], the Hamiltonian of the interaction between the molecule and the adsorption site can be represented in the form

$$H_s = -1/2\alpha q^2/R^4 + (qQ/R^3 - \gamma q^2/3R^4)P_2(\cos\theta), \quad (7)$$

where q is the point charge, R is the fixed distance between the molecular center of gravity and the charge, Q is the quadrupole moment in a molecule fixed coordinate system, and $P_2(\cos\theta)$ is the Legendre polynomial.

In strong electrostatic fields, the wave function of a disturbed state can be written in the form [11]

$$\Psi_{vJm} = \sum_{J'} a_{J'}^{vJm} \phi_{vJ'm}, \quad (8)$$

where $\phi_{vJm} = \chi_{vJ}(r)Y_{Jm}(\theta\phi)$, $\chi_{vJ}(r)$ is the vibrational wave function, v is the vibrational quantum number, and $a_{J'}^{vJm}$ are coefficients that provide a diagonal form of the Hamiltonian matrix (7) of the interaction between the molecule and the adsorption site.

The matrix was diagonalized by a numerical method. In this case, at least three higher levels and all lower levels of the same parity were mixed with the rotational level to be calculated. Corrections to the vibrational energy levels (ΔE_{vJm}), the space between which is much greater than that between the rotational levels, were calculated in accordance with the perturbation theory.

Table 3. Frequencies of the vibrational and vibrational–rotational transitions allowed by selection rules for hydrogen and deuterium

Transition*	H_2	D_2
00 ⟶ 00	**4101**	**2951**
00 ⟶ 20	**4692**	**3394**
00 ⟶ 2 ± 1	**4553**	**3241**
10 ⟶ 10	4108	2954
10 ⟶ 1 ± 1	3860	2746
1 ± 1 ⟶ 10	**4344**	**3152**
1 ± 1 ⟶ 1 ± 1	**4096**	**2950**
10 ⟶ 30	4691	3334
10 ⟶ 3 ± 1	4630	3249
1 ± 1 ⟶ 30	**4927**	**3538**
1 ± 1 ⟶ 3 ± 1	**4866**	**3452**
1 ± 1 ⟶ 3 ± 2**	–	–

* Transitions that will be observed in the spectra measured at a boiling temperature of nitrogen (77 K) are printed in boldface.

** Data on the energy of the 3 ± 2 level were not reported in [8].

To explain an experimentally observed decrease in the frequency of stretching vibrations of the H–H (D–D) bonds of adsorbed $H_2(D_2)$ molecules due to the Stark effect, which is 63 cm^{-1} (45 cm^{-1}), we should assume that the molecular center of gravity is at a distance of 3 Å from the adsorption site. This distance is approximately equal to the sum of the cationic radius of barium (1.35 Å [9]) and the kinetic radius of the H_2 molecule (1.6 Å [9]). In this case, the electrostatic field with a strength of 1.6×10^8 V/cm acts on the coordinated molecule. As estimated in [9], field strengths of the same order of magnitude are produced in faujasites at S_{II} sites spaced by a distance equal to the kinetic radius of a hydrogen molecule from the cation that balances the charge.

In these strong electrostatic fields, the number J is not a "good" quantum number, and the molecular rotation of H_2 and D_2 can be characterized by only the projection of the angular moment M onto the field direction [11]. Nevertheless, we will use the number J in the subsequent discussion below to describe vibrational–rotational energy levels in the strongly hindered rotation of *ortho*-hydrogen and *para*-hydrogen, implying that a given level grades into a level with the specified J at low barriers of hindered rotation.

In an electrostatic field with a strength of 1.6×10^8 V/cm produced by a single-point charge, the vibrational–rotational energy level of the ground state of H_2 and D_2 molecules with $J = 1$ and $M = \pm 1$ lies lower than the level with $J = 1$ and $M = 0$ by ~200 cm^{-1} [11]. Therefore, at the boiling point of nitrogen, only the lowest vibrational–rotational levels of *ortho*-hydrogen and *para*-hydrogen with $J = 1$ and $M = \pm 1$ are occupied.

Table 3 summarizes the frequencies of vibrational–rotational transitions allowed by selection rules for a mixture of the ortho and para isomers of hydrogen and deuterium adsorbed at 77 K, as calculated from the tabulated data [11] for the electrostatic field of a positive unit charge with the strength 1.6×10^8 V/cm.

We compared the experimental frequencies of the absorption band maxima in the spectra of adsorbed hydrogen and deuterium (Table 1) with the values calculated on the basis of the Stark effect (Table 3). This comparison demonstrates that both a 60-cm^{-1} decrease in the frequency of stretching vibrations of the H–H bond in the H_2 molecule coordinated to the Ba^{2+} cation and the vibrational–rotational structure of the IR spectra can be displayed taking into account the effect of a strong electrostatic field on the molecule. Thus, the splitting of vibrational–rotational absorption bands into two and four components and the appearance of absorption bands with maxima at ~4600, ~4800, and 4950 cm^{-1} for *para*-hydrogen and *ortho*-hydrogen, respectively, can be explained. Moreover, it becomes clear why the absorption band of stretching vibrations of the H–H bond was split by ~5 cm^{-1} in the spectrum of an adsorbed equilibrium mixture of *para*-hydrogen and *ortho*-hydrogen, which was observed previously in the

adsorption of H_2 on zeolites CaNaA [18, 19] and NaY [4], and why low-frequency absorption bands appeared in the region 4300–4400 cm^{-1} in the spectrum of *ortho*-hydrogen (the $1 \pm 1 \longrightarrow 10$ transition). It is likely that an absorption band at 4420 cm^{-1} corresponds to this transition.

CONCLUSION

Thus, the model of a strong electrostatic field can adequately explain the main features of the vibrational–rotational spectra of adsorbed hydrogen and deuterium. At the same time, it cannot reproduce the absolute values of experimental frequencies of vibrational–rotational transitions for *ortho*-hydrogen and *para*-hydrogen adsorbed on zeolites with an adequate accuracy. It is likely that more adequate models of the adsorption complexes should be used for this purpose, and the real configuration of electrostatic fields produced by both exchanged cations and framework oxygen anions in the zeolite cavities should also be considered. Probably, this will provide an opportunity to determine the true symmetry and the height of potential barriers of hindered rotation for coordinated molecules and to calculate more accurately the vibrational–rotational spectra of hydrogen and deuterium adsorbed on cationic forms of zeolites. The effect of hindered rotation on the vibrational–rotational levels of hydrogen has been previously considered in detail in [10, 20–22].

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