MODEL CALCULATION FOR SELECTIVITY OF TYPE A ZEOLITES IN THE ADSORPTION OF ISOTOPIC HYDROGEN MOLECULES. HENRY'S LAW REGION

V. S. Parbuzin and A. V. Larin

UDC 541.183

The possibility of utilizing adsorption methods for the purification, analysis, and production of hydrogen isotopes of high isotopic purity in the gas phase [1-6] required that the necessary theoretical apparatus be developed by combining phenomenological [1, 7] and statistical-thermodynamic approaches [1, 8]. An integral part of the latter is the model calculation of the Henry's law constants and the distribution coefficients used in engineering calculations for the corresponding adsorption apparatus.

The reliability of theoretical predictions depends to a substantial degree on the trustworthiness of the description of the two interaction subsystems considered in the calculation, the adsorbent and the adsorbate. Recently, thanks to the development of new experimental methods and the acquisition of new data, it has become possible to improve the trustworthiness of theoretical calculations by eliminating a number of assumptions, the most important of which are the assumptions about the magnitudes of the charge, polarizabilities, and radii of the ions of the zeolite lattice [9, 10]. As shown in [11], the degree of ionicity and the charge relationships of the zeolite lattice ions determine the magnitudes of the shifts of the transition bands of diatomic molecules adsorbed on type A zeolites. The availability of experimentally determined shift values [13-15] allows us to determine the radius and polarizability of ions as functions of the charge resulting from their degree of ionicity, which is determined by comparing the calculated and the experimental magnitudes of the shifts.

In the present work we report the results of utilizing the IR spectra of adsorbed diatomic molecules of hydrogen H_2, deuterium D_2, and nitrogen N_2 to determine the characteristics of the lattice ions of type A zeolite in its Na and Ca forms. We have used the data in [13-15] to make theoretical calculations of the distribution coefficients of mixtures of H_2 and D_2 and the characteristics of the adsorption of the monoatomic gases Ne and Ar in the region of the lowest degrees of surface coverage where it is comparatively simple to calculate the magnitudes of the heats of adsorption and the Henry's law constants [10]. The results of calculations made to determine these values in the region of moderate degrees of coverage will be presented in a later communication.

The potential energy calculations for the adsorbent—adsorbate interaction were made using the interaction terms in the form indicated in [1], so that we shall review some of the factors that distinguish this work from [1, 9, 10].

We considered the range of degree of ionicity 1

$$1\leqslant q_0\leqslant 5\ \ (q_0=q(\mathrm{Na})+q(\mathrm{Al})+q(\mathrm{Si})=|q(\mathrm{O_I})+q(\mathrm{O_{II}})+2q(\mathrm{O_{III}})|).$$

in which the degree of ionicity and ionic radius are considered to be continuous functions of ionic charge. The radii of all the lattice ions are given by a linear function of the magnitude of the charge of the ion, the constants of which are given in Table I. For estimating the polarizability of oxygen ions we used a linear dependence on the magnitude of the charge [10], the change in the polarizability of Si and Al with change in charge was described following the results in [16] by a function of the type $A\exp\{-[q(T)-B]^2/C\}$, where the constants A, B, and C are given in Table 2, and T is Si or Al.

Since the structure of $Na_{12}A$ zeolite is best refined with space group Fm3c [17, 18], the coordinates of the ions correspond to positions obtained from x-ray diffraction data interpreted in terms of the symmetry group Fm3c [18]. The coordinates of the ions of 1/16 of the volume of the α cell are given in Table 3 in a coordinate system having its axes oriented along the fourth-order axes of the cube describing the α cell.

M. V. Lomonosov Moscow State University. Translated from Vysokochistye Veshchestva, No. 1, pp. 101-109, January-February, 1988. Original article submitted July 7, 1987.

TABLE 1. Constants for the Dependence of the Radius of the Ion X on the Charge $r(X) = a - bq(X)$

X	a, Å	b, Å a.u. of charge^{-1}
O	1,15	0.76
Al	1,11	0.38
Si	1,18	0.55
Na	1,54	1.06

TABLE 2. Parameters for the Dependence of the Polarizability of Si and Al on Charge $q(T)$ $A \exp\{-[q(T) - B]^2/C\}$

Ion	Polarizability, a.u.^{3}			A	B	C
	$q=0$	$q=1$	$q=2$			
Si	39.61	13.84	5.36	0,109	−10,70	−19,40
Al	38.29	11,05	3,54	0,013	−12,39	−19.13

TABLE 3. Coordinates of the Ions of the Lattice of Zeolite $Na_{12}A$ [14]

Ion	X	Y	Z
Na_{I}	−6,9786	−6.9786	−6.9786
Na_{II}	−1,8045	−1.5544	−11.6001
Na_{II}	−6,6816	−6.6816	0
O_{I}	−11,6001	−5.2743	−0,1564
O_{II}	−11,6001	−4.8911	−4.8298
O_{III}	−9.1042	−8.8787	−3.6415
Si	−11,6001	−7.2774	−3.0165
Al	−11,6001	−2.9163	−7.4045

Table 1 gives the dimensions of the ions used to construct the linear relationship between the ionic radius and the charge. Because the greatest contribution to the value of the energy of repulsion comes from the interaction of the terms including the oxygen ions, the size of the radius of the oxygen atom $r(O^\circ) = a$ was allowed to vary as $r(O^\circ) = a - qb$. The upper limit for the region of variation of the radius of the oxygen atom was the radius at which there is no overlap of the spheres of the ions of the oxygen forming one tetrahedron TO_4. The boundary is different for the silica and the alumina tetrahedra and is 1.29 to 1.40 Å, respectively, for Si–O and Al–O distances of 1.597 and 1.731 Å [18].

As shown by calculations made in the two versions represented in Table 4, a change in the magnitudes of the dispersion and repulsion components of the energy of interaction when the Si and Al ions are taken into account are 30 and 4% of the magnitudes obtained without taking the Si and Al ions into account at the point of the minimum potential energy. Therefore, the calculations were made taking the interaction terms with the Si and Al ions into account for all the components of the interaction energy.

For the repulsion component of the interaction energy, expressions were proposed that correct for the anisotropic nature of the interaction between the ion and the X_2 molecule in the approximations of one- (1) and two-center (2) interactions:

$$E_{\mathrm{rep}} = \sum_i (B_i^{\parallel} \cos\theta_i + B_i^{\perp} \sin\theta_i) R_{icm}^{-12},$$

$$E_{\mathrm{rep}} = \sum_i (B_i^{\parallel} \cos\theta_i + B_i^{\perp} \sin\theta_i)(R_{i1}^{-12} + R_{i2}^{-12}),$$

where $B_i^{\perp}$ and $B_i^{\parallel}$ are the repulsion constants of the ion–molecule pair along the axes of the molecule perpendicular and parallel to the axis joining the centers of mass of the molecule and the ion. The dimensions of the X_2 molecule necessary for determining the repulsion

TABLE 4. Effect of Incorporating the Terms of the Interaction with Si and Al Ions in the Dispersion and the Repulsion Components on the Magnitude of the Potential Energy of the Interaction at $q_0 = 3.25$, $f_1 = f_2 = 1$

Coordinates θ, Φ, deg	R, a.u.	Components of PE·10^3, a.u.			
		incorporating Si and Al		disregarding Si and Al	
		$-E_{disp}$	E_{rep}	$-E_{disp}$	E_{rep}
3,9270	3.5	1.475	0,219	1,131	0.214
0,9553	4,3	1.771	0,451	1.369	0,441
	5,1	2.215	0.955	1,726	0,937
	5,9	2.885	2,090	2.269	2,053
	6,7	3,935	5,264	3,131	5,184
3,1416	3,5	1,433	0.136	1,091	0,130
0.7854	4.3	1,702	0.250	1.301	0,240
	5.1	2.114	0,524	1.622	0.503
	5.9	2.764	1,251	2.127	1.202
	6.7	3.822	3.338	2,949	3,211

TABLE 5. Potential Energy of the Interaction $H_2/Na_{12}A$ along the Different Axes C_n and Orientations

n	θ.Φ, deg	R, a.u.	$-E \cdot 10^3$, a.u.		
			orientation*		
			1	2	3
3	3.9270	3.5	1.721	2.699	1,674
	0.9553	4.3	2.054	3,373	1,765
		5.1	2.250	4.132	1,821
		5.9	1.892	4.721	1,688
		6.7	−2.112	3.968	0,316
2	3.1416	3.5	1.910	1.212	1.924
	0.7854	4.3	2.150	1,265	2,149
		5,1	2.271	1,287	2,387
		5.9	1.894	1.156	2,447
		6.7	−2.434	0.346	1.661
4	3.1416	3.5	1.931	0.739	2.223
	1.5708	4.3	2.165	0.670	2.493
		5.1	2.172	0.583	2,736
		5.9	1.519	0.270	2,709
		6.7	−1.038	−1.364	−1,312

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*Orientation 1 — axis of the molecule is directed along the axis of the motion of the center of mass of the molecule away from the center of the α cell; orientations 2 and 3 — the axis is perpendicular to the direction of motion, and the axes of the molecules in orientations 2 and 3 are perpendicular to each other (in the case of C_4, the angle between them is π/4).

constants were determined for the value of the Lennard-Jones radius under the condition that the volume of a spherical molecule of radius r_m is equal to the volume of a spherocylindrical or ellipsoidal model of the molecule. The results of the calculations for different models of the molecule are given below.

We evaluated the magnitude of the interaction of hexadecapole moment of the X_2 molecule with the third derivative of the field, according to an expression for the energy of electrostatic interaction from [19]. For values of the moments of 0.42 a.u. [20] and −7.504 a.u. [21] for H_2 and N_2, respectively, the contributions of these interaction terms are ~0.02 and 2.0% of the magnitude of the interaction energy (approximately $4.3 \cdot 10^{-3}$ a.u. and $6.1 \cdot 10^{-3}$ a.u.). In describing the experimental data obtained with a precision of 1 $cm^{-1} = 4.57 \cdot 10^{-6}$ a.u., the term for the interaction of the hexadecapole moment with the third derivative of the field is corrected for in calculating the potential energy of the N_2 molecule and is not corrected for in the case of H_2 and D_2, where it is of the order of the experimental error [13-15].

The corresponding calculations of the potential energy of the interaction of H_2, D_2, and N_2 molecules with the zeolite lattice in the vibrational states v = 0, 1 were made under

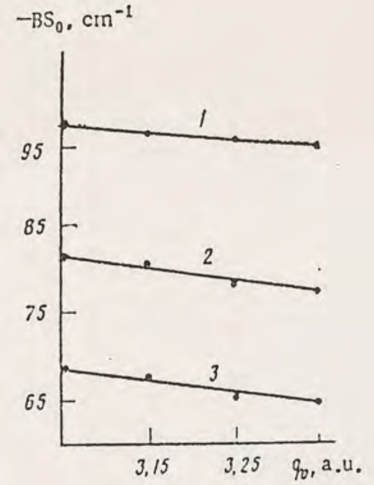

Fig. 1

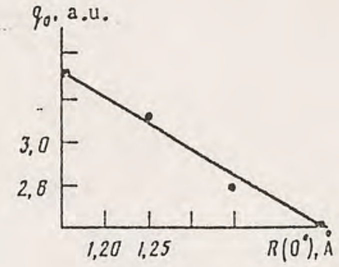

Fig. 2

Fig. 1. Dependence of the magnitude of the band shift of a "hard" molecule BS_0 on the degree of ionicity of the zeolite q_0 for different charge ratios of the oxygen ions f_1 and f_2: 1) $f_1 = 1.25$, $f_2 = 0.75$; 2) $f_1 = 1.00$, $f_2 = 1.00$; 3) $f_1 = 0.75$, $f_2 = 1.25$.

Fig. 2. Degree of ionicity q_0 at which the experimental value of the band shift is reproduced as a function of the radius of the oxygen atom for $f_1 = f_2 = 1.0$.

the assumptions made above. For determining possible adsorption sites, the potential energy was calculated for $v = 0$ for three orientations of the molecule relative to the direction of the motion of the center of mass of the molecule away from the center of the zeolite cell. The results obtained for the computations of the potential energy are given in Table 5. The relative positions of the minima depend on the ratio of the charges of the ions of the same sign, which are expressed here by $f_1 = q(O_{III})/q(O_{II})$ and $f_2 = q(O_I)/q(O_{II})$. When the parameters are allowed to vary within the limits $0.89 \leq f_1 \leq 1.12$ and $0.89 \leq f_2 \leq 1.12$, the deepest minimum remains on the third-order axis next to the Na_{III}^+, so that the value of the shift of the band of the fundamental transition $H_2/Na_{12}A$ was calculated at this location. The estimation of the boundaries of the intervals of the quantities f_1 and f_2 corresponds to the results obtained in [22] for the oxygen ions of the ring for Si:Al = 1. The orientation of the molecular axis is parallel to the edge shared by the six- and four-membered rings, next to the latter of which the Na_{III}^+ ion is located. We should mention the basic assumptions under which the magnitudes of the band shifts were calculated. The model of a six-dimensional harmonic oscillator was used to describe the magnitude of the band shifts. The use of the harmonic-oscillator approximation to describe the motion of the center of mass of the molecule in terms of angular variables is justified because the changes in the energies of the ground states of the motion of the center of mass associated with the intermolecular vibrational transition $v = 0 \rightarrow v' = 1$ with change in angle are small. Since the barriers to rotation of the molecule relative to the surface are high compared to the difference between the energies of molecular free rotation ($J = 0, 1$), the description of the energy of the two lower states is made using the harmonic-oscillator approximation. The total band shift which also includes the change in the frequencies of the hindered rotation associated with the intermolecular transition $v = 0 \rightarrow v' = 1$, represents the difference in the potential energies of the molecules interacting with the lattice ions in different vibrational states of the molecule. That the magnitude of the band shift depends on the degree of ionicity of the zeolite q_0 was demonstrated in [11]. In order to describe a number of other effects governing the magnitude of the band shift (BS) we shall represent it as the sum of two terms ($BS = BS_0 + BS_1$), the first of which is the most important part of the quantity. The basis for doing this is provided by the possibility of representing the potential energy as a term determined by the interaction of a "hard" molecule with the zeolite lattice and a term that depends on the amplitude of the intramolecular vibration. In the expression of the corresponding operator for the potential energy of the interaction $V^{(v)}$ in Eq. (3) these components are associated with the first and the second terms, respectively, of the right-hand side of the equation:

TABLE 6. Effect of the Choice of Model of the H_2 Molecule on the Value of the Shift BS_0 and on Band Splitting[a] for the Transition $H_2/Na_{12}A$ for q_0 = 3.25, $f_1 = f_2 = 1$

Model[b]	Δ[c]	Semiaxis ratio	$-BS_0$, cm^{-1}	$-SB(\varepsilon)$, cm^{-1} [d]
E	0,55	1,255	75,8	6,0(5,5), 2,2(9,3)
E	0,5	1,230	74,9	5,3(5,0), 2,2(9,0)
E	0,45	1,201	75,9	5,9(5,2), 2,2(9,0)
S	0,55	1,264	84,3	6,8(5,1), 2,4(8,9)
S	0,5	1,238	82,7	5,9(4,7), 2,4(8,7)
S	0,45	1,212	83,1	6,5(4,9), 2,4(8,7)

[a] Changes in the libration frequencies $\Delta\omega_i^{01}$ for i = 1, 2.

[b] E – ellipsoid; S – spherocylinder.

[c] Models correspond to the ratio of the semiaxes (a, b) for E and S: $a = b + \Delta r_0$, where r_0 is the internuclear distance in the ground state.

[d] ε – root-mean-square deviation of the corresponding libration frequency.

TABLE 7. Effect of the Choice of Approximation Used in Calculating the Repulsion Energy on the Value of the Splitting of the Band (SB) $H_2/Na_{12}A$ for f_1 = 0.75, f_2 = 1.25

$R(O^0)$, Å	q_0, a.u.	BS_0[a] and $SB(\varepsilon)$[b], cm^{-1}	
		one-center (1)	two-center (2)
1.15	2.65	−86.3 −5.2(3.9), −2.7(8.6)	−80.2 6.4(2.2), 1.1(6.2)
1.25	2.45	−86.5 −5.1(4.7), −2.8(9.4)	−78.8 8.9(2.4), 1.1(6.5)
1.35	2.25	−86.7 −7.7(5.6), −2.8(9.9)	−78.2 11.9(2.7), 1.1(6.8)
1.45	2.00	−88.3 −5.0(6.3), −2.8(9.9)	−78.2 15.8(3.0), 1.1(6.9)

[a] Value of BS_0 is given instead of BS, since the value of BS_1 is approximately the same at all points whether expression (1) or (2) is chosen.

[b] See last note to Table 6.

$$V^{(v)} = k_0^{(v)} + \sum_{n=1}^{n_e} \frac{k_n^{(v)}}{n!} x^n, \tag{3}$$

where $x = r - r_v$ is the displacement of the nucleus of the molecule from the average internuclear distance r_v of the vibrational state; $k_n^{(v)}$ are the expansion coefficients of the expansion of $V^{(v)}$ in powers of x; and $(n_e + 1)$ is the number of terms in the series. The band shift can be represented in the form of the two corresponding terms BS_0 and BS_1. In what follows we describe the dependence of the value of BS_0, the band shift of the hard molecule, on the radius of the atoms of lattice oxygen, the model of the molecule, and the ratio of the charges of the oxygen ions of different types.

Figure 1 depicts the dependence of the value of BS_0 on the degree of ionicity q_0 for some different values of the ratio of the charges of the ions of the zeolite lattice for the case R(O°) = 1.15 Å. The change in BS_0 that occurs on the transition between the given limiting values of the charge ratios is greater than the experimental error, and additional information is required in order to establish an exact relationship between the charges of the ions of the sublattice. The value of the degree of ionicity q_0 at which the calculated value BS is equal to the corresponding experimentally observed value is described by a nearly linear function of the radius of the lattice oxygen, as shown in Fig. 2. The comparison of the models of the ellipsoid and the spherocylinder for different semiaxis ratios points to the small change in the degree of ionicity that makes it possible to describe the experimental value BS when the model of the molecule is changed. The results for R(O°) 1.15 Å are given in Table 6.

TABLE 8. Change of the Value of the Splitting of the Band for the Transition $H_2/Na_{12}A$ as a Function of the Values f_1 and f_2 for R(0°) = 1.15 Å, (0°) = 1.15 Å

q_0	f_1	f_2	BS, cm^{-1}	SB(ε)[a], cm^{-1}
2.45	0.75	1,25	−78.3	−5,2(3,0), −2,7(8,0)
3.15	1.00	1,00	−85.0	−5,6(2.4), −2,4(7,5)
5.25	1,25	0,75	−80.8	−6,7(2.5), −1,6(7,0)
Experiment			−79.2±1,0	−5,0±1,0 [15]

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[a] See last note to Table 6.

TABLE 9. Magnitudes of BS and SB of Diatomic Molecules Adsorbed on Type A Zeolites at R(0°) = 1.15 Å

Gas	q_0	f_1	f_2	−BS, cm^{-1}	SB(ε)[a], cm^{-1}
			$Na_{12}A$ zeolite		
H_2	2,45	0,75	1,25	78.3	−5,2(3,0), −2,7(8,0)
	2,65	0,75	1,25	78,1	−5,3(3,1), −1,8(8,8)
	2,85	0.89	1,12	80.4	−4,9(22.6), −2,1(12,0)
	3.35	1,00	1.00	82.9	−5,7(2,4), −1,6(8,2)
	Experiment			79.2±1.0	−5,0±1.0 [15]
D_2	2.65	0,75	1.25	65,1	−11,4(2.1), −4,6(8,1)
	Experiment			65.0±1.0	0,0 [15]
N_2	2,65	0,75	1.25	−13.5	−2,5(7,8), −2,1(10,0)
	2.65[b]	0,75	1.25	−11.1	−2.1(6.6), −1,9(9,0)
	Experiment			−12.0±1,0	2,5±1,0 [14]
			Na_4Ca_4A		
H_2	2.65	0.75	1.25	35.6	−9.8(56,0), −13.3(11,6)
2.65	~~1.00~~	0.75	1.25	63.9	−10,5(52,0), −14.6(10,2)
2.65	~~1.00~~	1.00	1.00	63.3	−11.0(56.0), −16,4(12.6)
	Experiment			68.7±1.0	−4.5±1.0 [15]
D_2	2.65	0.75	1.25	36.2	0,9(27,2), 2.0(7.6)
2.65	~~1.00~~	0.75	1.25	53.8	−3.6(28.5), 6.0(15.1)
	Experiment			54.0	0.0 [15]
N_2	2.85	0.75	1.25	−12.7	−2.3(9.3), 0.0(9,5)
	Experiment			−11.1±1.0	3.5±1.0 [14]

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[a] See note d to Table 6.

[b] R(0°) = 1.15 Å.

[c] r_m = 1.65 Å [25].

[d] r_m = 1.78 Å [26], Δ = 0.45 (Table 6) for a spherocylindrical model of the molecule.

The experimental value of the band splitting in the harmonic approximation can be expressed as

$$SB_i = hc\Delta\omega_i^{01}, \quad i=1,\ 2,$$

where $\Delta\omega_i^{01} = \omega_i^{(1)} - \omega_i^{(0)}$ is the change in the frequency of libration of the molecule relative to the fragment of zeolite in the perpendicular (i = 1) and parallel (i = 2) planes during the intramolecular vibrational transition $v = 0 \rightarrow v' = 1$. According to the results (Table 6), the value of the band splitting depends on the model of the molecule and changes within the limits of error of the calculation when the degree of ionicity and radius of the oxygen atom are allowed to vary (Table 7). Based on an analysis of the values of the band splitting obtained using Eqs. (1) and (2) to calculate the energy of repulsion for the interaction of H_2 molecules with the zeolite lattice, an expression was selected for calculating the value of the potential energy. Table 8 gives the values of the band splitting calculated using Eq. (1) and (2); by comparing them it becomes possible to describe the band splitting using exprsesion (1) for the value of the interaction repulsion energy in the case of H_2. We note that the range of values of the parameters (q_0, f_1, f_2) needed for assessing possible models of multimolecular adsorption on type A zeolite, in which the calculated values of the band shifts and band splitting agree with the experimental values, is narrower than the region determined by the band shift alone. As an example, the values of the band shifts and the band splitting obtained for the limiting values of f_1 and f_2 considered are

TABLE 10. Isosteric Heats of Adsorption and Henry's Law Constants for Ne ($T = 84.1$ K) and Ar ($T = 228$ K) on $Na_{12}A$ Zeolite at $f_1 = f_2 = 1$

Gas	Potential	q_0, a.u.	Q_{ads}, kcal/mole	K_H, at./(u.c.· Pa)
Ar	6–12	1,7	3.116	1,95
	6–8–12	2,45	3.036	1,73
	6–8–12	2,65 [a]	2,950	1.48
	Experiment		3,0±0.1	2,0±0,4 [27]
Ne	6–12	3,1	1,111	5,33
	6–12	3,25	1,077	4,42
	6–12	3,4	1,047	3.71
	6–8–12	3,5	1,218	9,00
	6–8–12	3,7	1.187	7,58
	6–8–12	3,4 [b]	1,209	8,72
	Experiment		1,1±0,1	4,6±1,0

[a] $f_1 = 0.75$, $f_2 = 1.25$.

[b] In the cases given above for calculations made using a 6–8–12 potential we used $C_8^{Ne} = 106.1$ and $C_8^{Ar} = 1596.0$ a.u.·br^8, which were determined from the similarity ratio of the complex C_8/C_6R^2, and in the given case $C_8^{Ne} = 57.1$ [28]. For Ar the agreement of the calculated and the experimental values $C_8^{Ar} = 1692.9$ [29] is better, and the result is given for the former quantity.

given in Table 9 which shows that for $f_1 = 1.25$ and $f_2 = 0.75$ the value of the band splitting differs from the experimental value.

The relationship of the quantities $f_1 \leq f_2$ is confirmed by an analysis of the value of the $N_2/Na_{12}A$ band shift. For $f_1 \leq f_2$ in the intervals used in [22] the potential energy minima for the interaction of N_2 molecules correspond to a position on the second-order axis when the axis of the molecule is oriented parallel to the edge of the cube describing the α cell. In this position the value of the band shift obtained theoretically is in agreement with experiment. For $f_1 \geq f_2$ the deepest potential energy well for the interaction is at the location for H_2 on the same axis of the molecule. In the latter case the potential energy of the interaction of the quadrupole moment of H_2 with the field gradient is positive and does not allow the value of the band shift of $N_2/Na_{12}A$ to be described in the approximation we have been using.

The results of calculating the values of the band shifts and band splittings for molecules adsorbed on zeolites $Na_{12}A$ and Na_4Ca_4A are summarized in Table 9. The calculations of the band shifts and band splittings for molecules adsorbed on Na_4Ca_4A zeolite were made assuming an unchanged position of the lattice ions as compared with $Na_{12}A$ zeolite and the position of the Ca^{2+} ions in the position of the Na_I^+ ions. The position of the deepest potential energy well for the interaction of H_2 with the Na_4Ca_4A zeolite lattice corresponds to a point on the second order axis of the cube describing the α cell. The value of the H_2/Na_4Ca_4A band shift obtained under these conditions corresponds to the experimental value when the degree of ionicity $q_0 = 1.00$, differing from the value $q_0 = 2.65$ ($f_1 = 0.75$, $f_2 = 1.25$) at which the calculated value of the band shift for H_2, $D_2/Na_{12}A$ agrees with the experimental value. Apparently, the assumptions made about the structure of Na_4Ca_4A are too crude, and it is preferable to use data obtained at $2.65 \leq q_0 \leq 3.25$ ($f_1 \leq f_2$) to describe the characteristics of the ions of the Na_4Ca_4A lattice.

In order to compare the thermodynamic data obtained using the characteristics of the ion satisfying the conditions above with experimental data, we calculated the distribution coefficient of a mixture of H_2 and D_2 and the thermodynamic characteristics of Ne and Ar adsorption. The harmonic-oscillator approximation we used to describe the energy of the lower states of the hindered rotation of a molecule relative to a lattice fragment does not produce a correct description of the energy for higher states. Taking into consideration that the symmetry of the potential-energy surface for the interaction between the molecule and the zeolite lattice in the neighborhood of the probable adsorption site at low degrees of surface coverage (on the O_3 axis) is of the form $\lambda \cos^2 \nu + \mu \cos^2 \varphi$ (due to the presence of a Na_{III}^+ ion close to the given minimum), we compared the value of the experimental distribution coefficient at a temperature of $T = 90$ K ($\alpha_{H_2}^{D_2} = 3.3$) [23] with that calculated using the approximation of MacRury and Sams [24] at the values $\lambda = 24.9$ and $\mu = 5.42$ determined in the calculation. The theoretical value of $\alpha_{H_2}^{D_2} = 3.55$ is in good agreement with the experimental value.

The results, obtained in calculating the thermodynamic characteristics of the adsorption of Ne and Ar given in Table 10 using a 6–8–12 potential for the interaction of an atom with a lattice ion, allow us to describe the experimental values of the characteristics of the adsorption of Ne and Ar closer to the corresponding values of q_0 at which the experimental characteristics of the adsorption of Ne and Ar are reproduced using a 6–12 potential (in both cases the first term of the series for the induction component of the energy of the interaction was used).

Thus, a system has been proposed for using spectroscopic data to determine the characteristics of the lattice icns of a type A zeolite, and results are presented of calculations of the thermodynamic characteristics of adsorption that are in satisfactory agreement with experiment, at values of the lattice ion parameters determined in this work.

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