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IR SPECTROSCOPIC ESTIMATION OF THE BINDING ENERGIES OF WATER MOLECULES ADSORBED ON DISPERSED SYSTEMS.

PART 3. γ-Al_2O_3

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There are three modes of interaction between water molecules and centers in γ-Al_2O_3, which arise from marked differences in hydrogen-bond energy.

γ-aluminum oxide is a classical adsorbent with an extensively hydroxylated surface. It has a defective cubic spinel lattice with space group Fd3m, while the vacant cation sites in a tetrahedral environment are stabilized by hydroxyl ions.

We have examined the structure of adsorbed water by IR and nuclear magnetic resonance methods, as well as by direct measurement of the bound water density. These methods require data on the structure and disposition of the active surfaces, and these were obtained (Fig. 1) as follows.

The coordinates of the oxygen and aluminum atoms within the unit cell (7.895·7.895 Å) in projection on any plane were taken from [1], in particular on the (001) plane for space group Fd3m. However, an aluminum atom is always in an octahedral environment of oxygen atoms, and only a small proportion of these atoms have incomplete coordination, so the surface can be represented as consisting of oxygen atoms at two levels, as shown in Fig. 1. A feature of γ-Al_2O_3 is that some of the surface oxygen atoms are replaced by OH groups.

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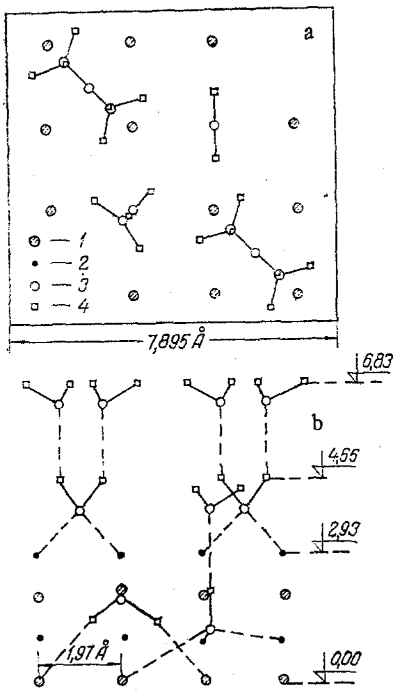


Fig. 1

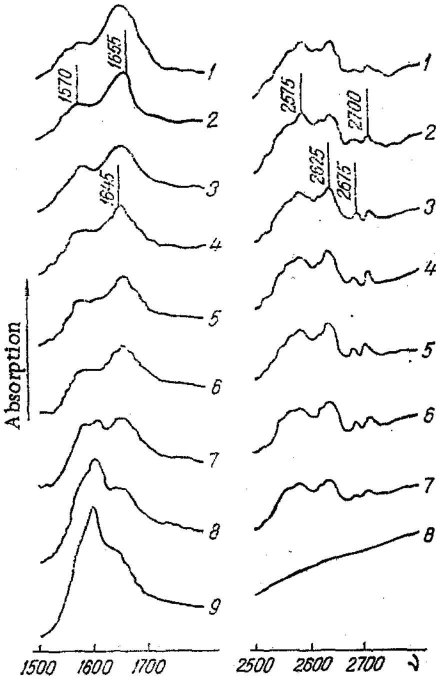


Fig. 2

Fig. 1. Surface structure of γ-Al_2O_3: a) in projection on the (001) plane; b) on the (100) plane; 1) oxygen; 2) hydrogen in the lattice surface; 3) oxygen; 4) hydrogen in adsorbed water molecules.

Fig. 2. Changes in IR spectra of water molecules adsorbed on γ-Al_2O_3 in relation to water content and temperature during desorption: 1) P = 4.35%; t = 20°C; 2) 4.35 and 65; 3) 4.35 and 90; 4) 3.57 and 125; 5) 3.57 and 140; 6) 3.57 and 160; 7) 3.0 and 190; 8) 1.0 and 200; 9) 0.0 and 220. ν, cm^{-1}.

To estimate the number of these, we used a derivative recording on heating the specimen up to 1000°C and determined the specific surface. The number of surface OH groups was calculated from

$$N_{(\mathrm{OH})} = \frac{2P_{(\mathrm{OH})} a_0^2 A}{MS}, \quad S = \frac{P_\mathrm{m}}{d_\mathrm{w}\, l}, \tag{1}$$

where $N_{(OH)}$ is the number of OH groups on one face of the unit cell; a_0, lattice parameter (a_0 = 7.895 Å); A, Avogadro's number; $P_{(OH)}$, mass of water per g of adsorbent released on heating from 200 to 1000°C; S, specific surface of 1 g; P_m, mass of the adsorbed water corresponding to coating of all the active centers (double-layer mass); d_w, density of the adsorbed water corresponding to P_m; l, projection of the length of the bond formed in an adsorption dimer on a plane perpendicular to the surface of the adsorbent; and M, molecular weight of water. In our case $P_{(OH)}$ = 0.0452 g/g, P_m = 0.095 g/g, d_w = 1.1 g/cm³, l = 4.66 Å, S = 185 m²/g, and then $N_{(OH)}$ = 9.

The number of adsorbed water molecules corresponding to 1% water content is given by

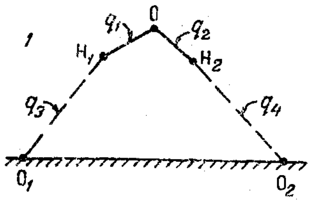
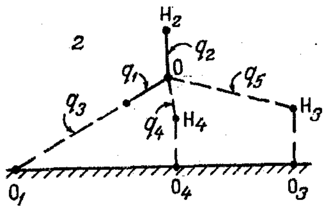
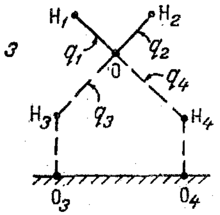
$$N_{(\mathrm{H_2O})} = \frac{P_\mathrm{m}\, a_0^2 A}{SM}, \tag{2}$$

and then $N_{(H_2O)}$ = 1.

IR spectroscopy was used to determine the orientations of the adsorbed water molecules with respect to the surface centers and the bond energies between the molecules and the latter.

The measurements have been described in detail in [2]; heavy water D_2O was used.

TABLE 1. Parameters of Water Molecules Adsorbed on γ-Al_2O_3

Interaction scheme, projection on the (001) plane		
		
frequency, cm^{-1}		
2675, 2575, 1655	2700, 2575, 1640	2675, 2625, 1570

angles between bonds, deg

∟ H_1OH_2	∟ O_1H_1O	∟ O_2H_2O	∟ H_1OH_4	∟ H_2OH_3	∟ H_2OH_4	∟ OH_1O_1	∟ H_3OH_4	∟ H_1OH_2	∟ H_1OH_3	∟ H_3OH_4
104,50	169,5	169,5	124,18	99,3	99,3	123,4	101,6	104,50	112,3	101,6

force constants, 10^6 cm^{-2}

$K_{q_1q_1}$	$K_{q_2q_2}$	$K_{q_3q_3}$	$K_{q_4q_4}$	$K_{q_1q_1}$	$K_{q_2q_2}$	$K_{q_3q_3}$	$K_{q_4q_4}$	$K_{q_5q_5}$	$K_{q_1q_1}$	$K_{q_2q_2}$	$K_{q_3q_3}$	$K_{q_4q_4}$
11,95	11,95	2,14	2,14	11,52	12,57	0,98	0,74	0,74	12,16	12,16	0,74	0,74

Figure 2 shows the changes in the IR spectra in the ranges 1500-1700 and 2500-2800 cm^{-1} for water adsorbed on γ-Al_2O_3 on desorption, while Table 1 gives the analysis results.

The basis for the analysis was the determination of the force constants of the O—D or O—H bonds from the stretching frequencies and of the force constants of the hydrogen bonds from the deformation frequencies.

Figure 1 and Table 1 show that there are three modes of interaction at the centers in γ-Al_2O_3: 1) a water molecule forms hydrogen bonds to two lattice oxygen atoms; 2) the oxygen in the molecule interacts simultaneously with two OH groups, while one of the hydrogen atoms interacts with a lattice oxygen atom; and 3) a water molecule is attached to two OH groups via the oxygen atom.

We thus get two symmetrical complexes and one unsymmetrical one.

The frequencies of the deformation vibrations were calculated from

$$\nu_{\alpha\alpha}^2 = D_{\alpha\alpha} + \sum_{\mu \neq \alpha} \frac{D_{\alpha\mu} D_{\mu\alpha}}{D_{\alpha\alpha} - D_{\mu\mu}}, \tag{3}$$

where $D_{\alpha\alpha}$, $D_{\alpha\mu}$, $D_{\mu\alpha}$, $D_{\mu\mu}$ are the total-interaction coefficients. Formula (3) has been derived by El'yashevich [3] from the secular equation subject to condition $|D_{\alpha\mu}| \ll |D_{\alpha\alpha} - D_{\mu\mu}|$. The interaction coefficients are as follows:

$$D_{\alpha\alpha} = \sum_{\lambda=1}^{r} A_{\alpha\lambda} K_{\lambda\alpha},\ D_{\alpha\lambda} = \sum_{\lambda=1}^{r} A_{\alpha\lambda} K_{\lambda\mu},$$
$$D_{\mu\alpha} = \sum_{\lambda=1}^{r} A_{\mu\lambda} K_{\lambda\alpha},\ D = \sum_{\lambda=1}^{r} A_{\mu\alpha} K_{\lambda\mu}, \tag{4}$$

where $A_{\alpha\lambda}$, $A_{\mu\lambda}$ are the elements in the coefficient matrix for the kinematic interaction and $K_{\lambda\alpha}$, $K_{\lambda\mu}$ are the elements in the force-constant matrix.

We use [2, 4] to derive the force constants for the interaction of a bond angle with itself, for the interaction between two bonds, the interaction of a bond angle with a bond, the angle formed with a hydrogen bond, the interaction between any angles having two or one common atoms, of a valency bond with a hydrogen-bond angle, of a valency angle with a hydrogen bond, and a valency bond with a hydrogen bond. The force constants for the interaction of a valency bond with itself and for a hydrogen bond with itself were determined by analyzing the frequencies.

The kinematic-interaction coefficients for any pair of coordinates were calculated from similar formulas, which are given in [2]. These formulas were derived from expressions for the natural vibrational coordinates for the planar vibrations of the water molecule (in the various schemes) are represented in terms of atomic displacements from the B matrices (the characteristic form of the B matrices is given in [2]).

The angles (natural vibrational coordinates) between the valency bonds and the hydrogen ones and between hydrogen bonds were calculated from the coordinates of the oxygen atoms and of the hydrogen in the water molecules adsorbed on the centers (Table 1). This shows that the bonds between the oxygen atoms in the water molecules and the lattice are kinked.

We determined the kinematic-interaction coefficients used in calculating the force constants for the hydrogen bonds from the deformation frequencies while incorporating the changes in the equilibrium bond lengths in the water molecule on the basis of (5), which was derived in [5]:

$$\frac{K_{(0-D)}}{K_{(0-D)_0}} = \frac{l_0^3}{l^3}, \tag{5}$$

where $K_{(o-D)_0}$ is the force constant of the O—D bond in the isolated water molecule, where its length is l_0, ($K_{(o-D)_0} = 12.87 \cdot 10^6$ cm^{-2}, $l_0 = 0.96$ Å), while $K_{(o-D)}$ is the force constant of O—D in an adsorbed water molecule, where the length is l.

One can also use (3) to calculate the O—D bond force constants in D_2O in the unsymmetrical complex, but it is found that the difference $D_{q_1q_1} - D_{q_2q_2}$ is close in magnitude to $D_{q_1q_2} \cdot D_{q_2q_1}$, so the frequencies and force constants were determined by solving the simple secular equation

$$\begin{vmatrix} D_{q_1q_1} - \nu^2 & D_{q_1q_2} \\ D_{q_2q_1} & D_{q_2q_2} - \nu^2 \end{vmatrix} = 0, \tag{6}$$

while neglecting the contributions from the diagonal and nondiagonal total interaction coefficients for the other bonds.

The following are the formulas for the antiphase frequency ν_{uf} and the synphase frequency ν_{sf} for vibration of the O–D bonds in the unsymmetrical complex derived from (6):

$$\nu_{uf} = \left\{\frac{1}{2}(D_{q_1q_1} + D_{q_2q_2}) + \frac{1}{2}[(D_{q_1q_1} + D_{q_2q_2}) - 4(D_{q_1q_1}D_{q_2q_2} - D_{q_1q_2}D_{q_2q_1})]^{1/2}\right\}^{1/2}, \tag{7}$$

$$\nu_{us} = \left\{\frac{1}{2}(D_{q_1q_1} + D_{q_2q_2}) - \frac{1}{2}[(D_{q_1q_1} + D_{q_2q_2})^2 - 4(D_{q_1q_1}D_{q_2q_2} - D_{q_1q_2}D_{q_2q_1})]^{1/2}\right\}^{1/2}. \tag{8}$$

In deriving the total-interaction coefficients, we neglected the products of the force constants by the kinematic coefficients, as these represented only small corrections.

It is evident [4] that the frequency difference in an unsymmetrical complex is larger than that in a symmetrical one. According to Fig. 2, $\nu_{uf} = 2700\ \text{cm}^{-1}$, $\nu_{sf} = 2575\ \text{cm}^{-1}$.

In a symmetrical complex, $D_{q_1q_1} = D_{q_2q_2}$, and then the solution to (6) takes the simple form

$$\nu_s^2 = D_{q_1q_1} - D_{q_1q_2},\quad \nu_{us}^2 = D_{q_1q_1} + D_{q_1q_2}. \tag{9}$$

It follows from [2] that the adsorption energy of a water molecule at two oxygen atoms (scheme 1) is greater than that at two OH groups (scheme 3). Then for interaction in scheme 1 we have from Fig. 2 that $\nu_s = 2575\ \text{cm}^{-1}$, $\nu_{us} = 2675\ \text{cm}^{-1}$, while for scheme 3 $\nu_s = 2625\ \text{cm}^{-1}$, $\nu_{us} = 2675\ \text{cm}^{-1}$.

When one varies some of the diagonal and nondiagonal force constants, one can derive the values from the frequencies found by experiment (Table 1). Three frequencies were found in the deformation region: 1570, 1640, and 1655 cm^{-1}. According to [2, 4], the increase in these frequencies is due to the increase in the number and energy of the hydrogen bonds, and it is also substantially dependent on increase in the O_1HO angle (where H is a hydrogen atom in the water molecule).

Consequently, 1570 cm^{-1} corresponds to the deformation vibrations of a water molecule adsorbed in scheme 3. From (3) we determine the force constants for $O–H_3$ and $O–H_4$ hydrogen bonds for this scheme: $K_{q_3q_3} = K_{q_4q_4} = 0.74 \cdot 10^6\ \text{cm}^{-2}$.

On taking these to be the same in scheme 2, and taking the frequency of the deformation vibrations as 1640 cm^{-1} in this scheme, we determine the force constant of the hydrogen bond between a lattice oxygen atom and hydrogen in a water molecule: $K_{q_3q_3} = 0.98 \cdot 10^6\ \text{cm}^{-2}$.

All the parameters are known for a water molecule adsorbed in scheme 1. We substitute these into (3) to get that the force constant of the hydrogen bonds are $K_{q_3q_3} = K_{q_4q_4} = 2.14 \cdot 10^6\ \text{cm}^{-2}$. According to [4] and other papers, the energy of a hydrogen bond is proportional to its force constant. Therefore, the adsorption energy of a water molecule forming bonds to active centers in scheme 1 is 1.75 times larger than that for scheme 2 or 2.9 times that for scheme 3.

These data have been used in examining the structure of adsorbed water by nuclear magnetic resonance.

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