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ON CHANGES IN THE STRUCTURE OF WATER DUE TO ITS CONTACT WITH A SOLID PHASE. II. IR-SPECTROSCOPY STUDIES

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The experimental data on vibrational spectra and the theory of polyatomic molecular vibrations have been used to determine the valence angle in water molecules adsorbed at active centers on a surface of the solids under study.

In [1], it has been shown that the longitudinal relaxation time in the NMR spectra of water molecules interacting with a surface of a solid phase differs from the same parameter for water in the absence of a solid phase. The experimental data obtained and the available analytical dependences have allowed the determination of the changes in distances between two spins in a H_2O molecule, those between oxygen atoms in two neighboring water molecules, the valence angle, and hydrogen bond energies in liquid water in contact with a solid.

Also, it has been established in [1] that the process of spin-lattice relaxation, in which a system of nuclear spins attains thermal equilibrium with other degrees of freedom of a test sample, is determined by the kinetic energy of nuclear vibrations. But in liquid water, the kinetic energy of nuclear vibrations will change with the valence angle in a H_2O molecule. It is quite obvious that the change in the valence angle of a molecule in a volume is caused by its adsorption on active sites of a solid surface, i.e., during adsorption the H_2O molecule deforms and, passing into a volume, retains the traces of this deformation.

The present communication reports the results of valence angle determination in a H_2O molecule adsorbed on a surface of upper Cretaceous silica, γ-Al_2O_3, and montmorillonite. The results are obtained from the data on experimental vibrational spectra and from calculations using the theory of polyatomic molecular vibrations.

The experimental technique and measurement procedure were the same as in [2]. Figure 1 exhibits the spectrum of H_2O adsorbed on silica powder prepared without vacuum at a temperature of heating determined by a globar lamp. Under vacuum conditions, the spectrum disappears at the same temperature. Whence it is obvious that the bonding energy (the bonding diagram is given in Fig. 3) of H_2O molecules with active centers of silica surface is insignificant. As seen from Fig. 1, the frequencies from 1300 to 1500 cm^{-1} within the region of deformation vibrations and their overtones in a range of 2700 to 3000 cm^{-1} have been found. The maximum of the band in the region of deformation vibrations is at 1458 cm^{-1}.

To analyze this frequency, we use the formula

$$\nu_{\alpha\alpha}^2 = D_{\alpha\alpha} + \Sigma \frac{D_{\alpha\mu} D_{\mu\alpha}}{D_{\alpha\alpha} - D_{\mu\mu}} . \qquad (1)$$

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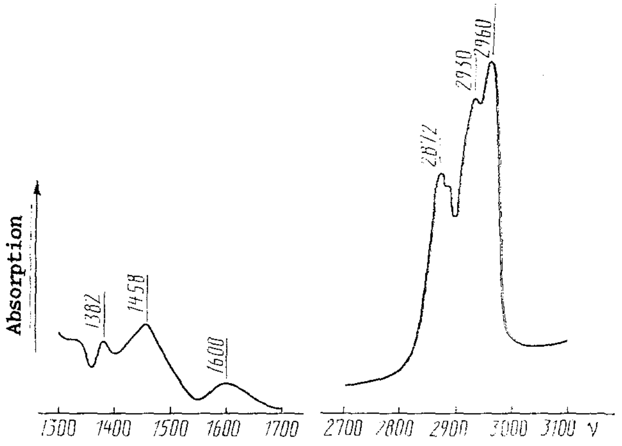

Fig. 1. IR-spectra of water adsorbed on a disperse silica surface. ν, cm^{-1}.

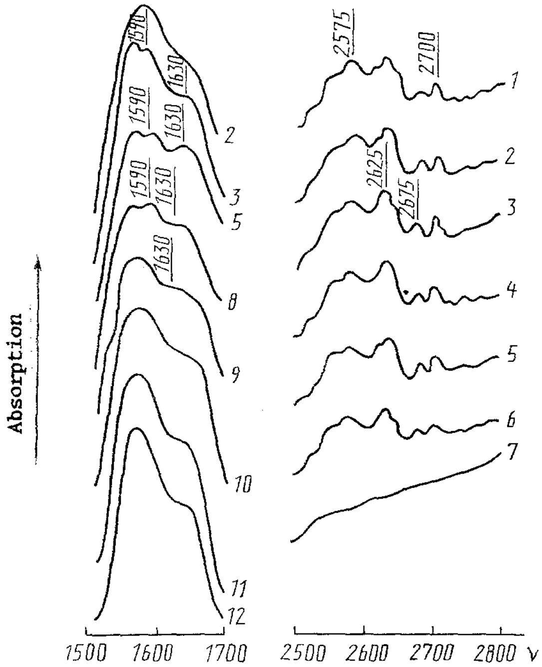

Fig. 2. Change in IR-spectra of γ-Al_2O_3 during water desorption: 1) sample heating temperature 65°C; sample humidity 4.35%; 2) 90 and 4.35; 3) 125 and 3.57; 4) 14 and 3.57; 5) 160 and 3.57; 6) 190 and 3.0; 7) 200 and 1.0; 8) 220 and 0.0; 9) 240 and 0.0; 10) 260 and 0.0; 11) 290 and 0.0; 12) 330 and 0.0.

The formula (1), derived by M. A. El'yashevich [3], is based on the secular equation, provided that $| D_{\alpha\mu} | \ll | D_{\alpha\alpha} - D_{\mu\mu} |$. The quantities $D_{\alpha\alpha}$, $D_{\mu\alpha}$, $D_{\mu\alpha}$, and $D_{\mu\mu}$ are called the coefficients of total interaction. They are obtained as follows:

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

$$D_{\mu\alpha} = \sum_{\lambda=1}^{r} A_{\mu\lambda}K_{\lambda\alpha}, \quad D_{\mu\mu} = \sum_{\lambda=1}^{r} A_{\mu\lambda}K_{\lambda\mu}, \tag{2}$$

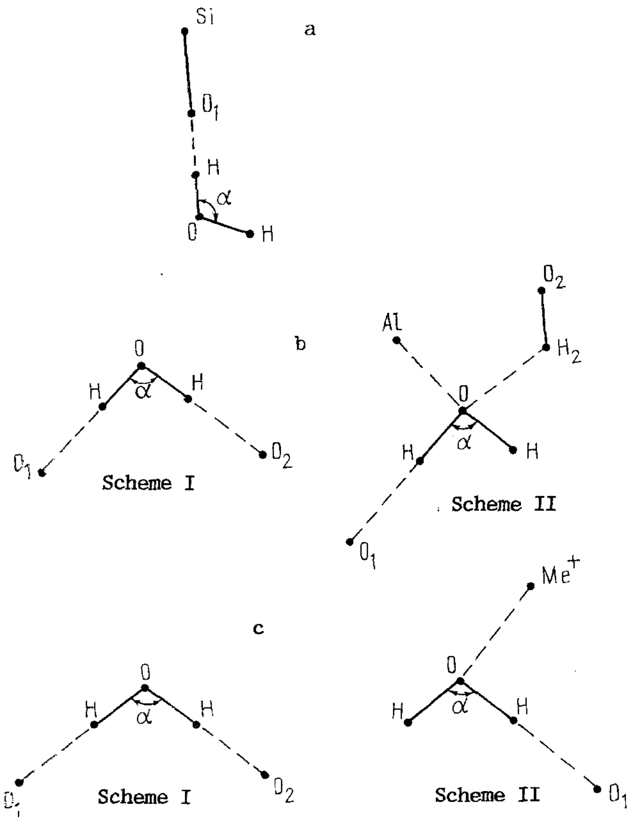

Fig. 3. Interaction schemes of water molecules with active centers of a solid surface: a) silica; b) γ-Al_2O_3; c) montmorillonite.

where $A_{\alpha\lambda}$ and $A_{\mu\lambda}$ are the elements of the matrix of kinematic iteration coefficients, and $K_{\lambda\alpha}$ and $K_{\lambda\mu}$ are the elements of the matrix of force constants.

The kinematic coefficients were calculated by formulas given in [2, 4].

The values of the force constants were taken from [5], with the exception of the force constant of interaction of the valence angle with itself, which was calculated as a function of the valence angle α by the formula obtained in [6]:

$$\frac{K_{\alpha\alpha_0}}{A_{\alpha\alpha_0}} = \frac{K_{\alpha\alpha}}{A_{\alpha\alpha}}, \tag{3}$$

where

$$A_{\alpha\alpha} = \frac{6\sin^2\alpha\,(1-\cos\alpha)^{-1} - 4\cos\alpha}{\sqrt{2(1-\cos\alpha)^3}}.$$

In formula (3), $K_{\alpha\alpha 0}$ and $A_{\alpha\alpha 0}$ stand for an isolated H_2O molecule.

An analysis of the frequencies of deformation vibrations was reduced to the calculation of kinematic coefficients, $K_{\alpha\alpha}$, and the dynamic coefficients as functions of the valence angle. When the calculated and the experimental frequencies were equal, the valence angle in the water molecule adsorbed on a disperse silica surface was 113°. In accordance with [5], a scatter in values of an angle in a water molecule is $\approx$ (108 ± 10°).

Thus, during water adsorption on a silica surface the adsorbed H_2O molecules acquire another valence angle which is different from that for the molecule in a liquid or vapor volume. A continuous exchange occurs between the adsorbed molecules and the molecules in a volume, i.e., a continuous transfer of the deformed H_2O molecules into the liquid. Measuring the longitudinal relaxation times in NMR spectra, we have discovered traces of so-deformed molecules. In this case the degree of distortion of angle α diminishes with the decreasing mass of the solid phase in the system.

Owing to the presence of overtones in the spectrum of water adsorbed on silica powder, the possibility arises to develop an alternative approach to calculating angle α.

Following [4], we may write in the harmonic approximation the probability of a transition between the energy levels for which one of their quantum numbers differs by unity (fundamental oscillations); for a single event of interaction with a photon this probability is determined by the square of the quantity:

$$\left(\frac{\partial M_e}{\partial Q_i}\right)_0 \int \varphi_i' Q_i \varphi_i'' dQ_i = \left(\frac{\partial M_e}{\partial Q_i}\right) (v_i + 1)^{\frac{1}{2}} Q_{0i}, \tag{4}$$

while the probability of transition between energy levels with one quantum number changed by two (the first overtones) is characterized by the square of the quantity:

$$\left(\frac{\partial^2 M_e}{\partial Q_i^2}\right)_0 \int \varphi_i' Q_i^2 \varphi_i'' dQ_i = \left(\frac{\partial^2 M_e}{\partial Q_i^2}\right) [(v_i + 1)(v_i + 2)]^{\frac{1}{2}} Q_{0i}^2. \tag{5}$$

Provided that the stretching and deformation vibrations completely break up (this is the case with the spectrum of water adsorbed on silica powder), we may, also following [4], write:

$$\left(\frac{\partial M_e}{\partial Q_i}\right)_0 = \left(2\frac{\partial M_e}{\partial \alpha}\cos\frac{\alpha}{2} - \frac{M_e}{s}\sin\frac{\alpha}{2}\right) l_\alpha A_i, \tag{6}$$

$$\left(\frac{\partial^2 M_e}{\partial Q_i^2}\right)_0 = 2\left(\frac{\partial^2 M_e}{\partial \alpha^2}\cos\frac{\alpha}{2} + \frac{\partial M_e}{\partial \alpha}\,\frac{\sin\frac{\alpha}{2}}{s}\right) l_\alpha^2 A_i. \tag{7}$$

An overtone-to-fundamental oscillation frequency ratio is determined as

$$A = \frac{4(v_i + 2) Q_{i0}^2 \, l_\alpha^2 A_i \left(\frac{\partial^2 M_e}{\partial^2 \alpha}\cos\frac{\alpha}{2} + \frac{\partial M_e}{\partial \alpha}\sin\frac{\alpha}{2}\, s^{-1}\right)}{\left(2\frac{\partial M_e}{\partial \alpha}\cos\frac{\alpha}{2} - M_e s^{-1}\sin\frac{\alpha}{2}\right)^2}. \tag{8}$$

Substituting A, found from an experimental spectrum, into Eq. (8), yields α. But for this purpose we need to know $M_e = f(\alpha)$. This function will be presented in the next communication; here, we only note that for silica at $(M - m) \rightarrow p_0$, $(E_a - E_0)/(kT) = 0.693$.

Consider the results obtained for γ-Al_2O_3. This oxide is a classical adsorbent with a highly hydroxylated surface. It has a defective spinel cubic lattice with the space group Fd3m, and the valence sites of cations in a tetrahedral environment are stabilized by hydroxyl ions. Data on the structure and position of active centers on the surface of the lattice are given in [7, 8, 9]. The orientation of water molecules with respect to the active centers on the surface of the lattice and the binding energies of molecules with these centers have been established by IR-spectroscopy.

Now we turn to the works published earlier.

In [10], consideration is given to the change in the spectrum of γ-Al_2O_3 subjected to a thermal treatment in vacuum. Strong bands at 3470 and 1635 cm^{-1} pertain to water bound to the surface by hydrogen bonds which can be removed under vacuum at temperatures up to 150°C. The absorption bands at 1610 and 3550 cm^{-1} are assigned to water molecules coordinationally bound with Lewis acid centers. The removal of these water molecules takes place at 300°C. The Lewis centers in γ-Al_2O_3 are attributed to the surface defects which are threefold-coordinated with Al atoms with a vacant p-orbital.

In [10], it is shown that the adsorption of water molecules at small surface coverages occurs on Lewis centers (donor-acceptor interaction) and on a Brenstead center (a hydroxyl group).

In [11], the existence of 5-6 different types of OH-groups in a hydroxyl cover of γ-Al_2O_3, a large part of which interacts with each other to form hydrogen bonds of different strengths, is pointed out. In this case, deformation vibrations are found only at one frequency, i.e., 1625 cm^{-1}, that persists in the spectrum up to 300°C and disappears at 400°C. The authors think that such water molecules form donor-acceptor bonds with a coordinationally-unsaturated aluminium atom.

Figure 2 exhibits the changes in the IR-spectra of water adsorbed on γ-Al_2O_3 during the desorption in the region of 1500 to 1700 cm^{-1} and 2500 to 2800 cm^{-1} in our experiments. Inspection of this figure reveals two frequencies in the region of deformation vibrations, i.e., 1590 and 1630 cm^{-1} The former remains at the sample vacuum dehydration temperature of 220°C, while the latter persists up to 330°C. Therefore, it may be assumed that there exist two schemes of interaction of water molecules with active centers on the surface of a lattice (Fig. 3). Proceeding from the structure of these centers and the nature of dehydration of water molecules, we relate the water molecules that form hydrogen bonds with two oxygen atoms of a lattice to the first scheme, while the second scheme applies to the molecules whose oxygen atoms interact simultaneously with a coordinationally-unsaturated aluminium atom (a Lewis center) and with a OH-group (a Brenstead center) and one of the oxygen atoms interacts with an oxygen atom in the lattice.

An analysis of the frequencies in the region of deformation vibrations has allowed the determination of valence angles α for each interaction scheme. These calculations have also been made using a formula of [1]. But in order to determine the kinematic interaction coefficients, matrices B which express natural vibrational coordinates in terms of the displacement of atoms from an equilibrium position have been constructed [4].

It should be noted that by varying the valence angle in a water molecule we may reduce each of the above interaction schemes to any experimental frequency of deformation vibrations. Therefore, in order to relate any frequency obtained in experimental IR-spectra to one of these schemes, the following three principles must be taken into consideration:

1) a change of the valence angle in a water molecule to the moment of formation of a double adsorbed molecular layer (in this case the solid phase-to-entire system mass ratio tends to unity) must be larger than the changes of the same angle determined from measured longitudinal relaxation times for the solid phase-to-entire system mass ratio much less than unity;

2) the difference between the calculated frequency of deformation vibrations obtained for each established scheme of interaction at the valence angle of 104.5°, corresponding to an isolated water molecule, and the experimental frequency must be minimal;

3) the lifetime of those molecules on an adsorbent surface whose binding energies to active centers is weaker must be shorter.

Naturally, a direct calculation of the valence angle of an adsorbed molecule based on the interaction between valence electrons and lone-pair electrons of an oxygen atom and with a solid surface would most unambiguously permit us to determine the scheme responsible for each frequency. But for the time being, this is a difficult problems. In order to solve it, we evaluate the lattice deformations of solids in the process of water adsorption, i.e., the charge transfer in the "solid-adsorbed water" systems.

We now return to the calculation of the frequencies of deformation vibrations. The first and the third principles given above make it obvious that the valence angle in a water molecule in a volume is formed as a result of adsorption of these molecules according to scheme I. Therefore, the frequency of 1590 cm^{-1} pertains to scheme I. As seen from the spectrum, this frequency disappears at 220°C; therefore, a change in the force constant of the valence bond must be taken into account in the matrix of force constants. An analysis of the frequencies of stretching vibrations has allowed the calculation of the force constants of a valence bond. Here, the equations for a symmetric adsorbed complex given in [7] were used. For the frequency of 1590 cm^{-1}, the angle α proved to be 107°, and for $m/M \rightarrow 1$, $(E_a - E_0)/(kT) = 0.198$.

Consider scheme II. To this scheme of interaction of water molecules with active centers of γ-Al_2O_3 corresponds the frequency of 1630 cm^{-1}. As seen from the spectrum, this frequency disappears at 340°C; therefore, a change in the force constants of the valence bonds is taken into account in the matrix of force constants by means of the equation for a non-symmetric adsorbed complex given in [7].

For the frequency 1630 cm^{-1}, the angle α was 1043° and for $m/M \rightarrow 1$, $(E_a - E_0)/(kT) = -0.028$.

We now discuss the results obtained for montmorillonite (natural form). Montmorillonite is an argillaceous mineral with an expanding, under hydration, crystalline lattice. The basal surfaces of its lattice are formed by oxygen atoms, and the lateral faces by oxygen atoms and OH-groups. A silicate layer of montmorillonite possesses some negative charge in the case when its constituent, octahedral aluminium, is partially substituted for magnesium or a certain amount of silica is substituted for aluminium. The negative charge is neutralized by cations located between layers.

A number of works are known that are devoted to IR-spectroscopic studies of montmorillonite. Thus in [12] it is pointed out that the region of deformation vibrations displays a weak band with a frequency of 1640 cm^{-1} due to the water molecules of an external coordination sphere of exchange cations and a strong band at 1630 cm^{-1} due to water molecules directly interacting with exchange cations. Similar frequencies were also obtained in [13].

In [2, 14], the IR-spectra of the natural and the ion-substituted forms of montmorillonite in the region of stretching and deformation vibrations of adsorbed water were obtained by the authors. It is worthy to note that the frequencies between 1620 to 1640 cm^{-1} and between 1300 to 1315 cm^{-1} have been found within the region of deformation vibrations during the adsorption of H_2O and D_2O molecules, respectively, when both the degree of dehydration and the structure of the exchange cation are varied.

Proceeding from the available information on the positions of atoms in the surface layers of a montmorillonite lattice [15] and on the existence of frequencies in the region of deformation vibrations at a dehydration temperature above 50°C, two schemes of interaction of water molecules with active adsorption centers on these surfaces (Fig. 3) may be distinguished. The first scheme of interaction is related to water molecules that form hydrogen bonds with two oxygen atoms of the lattice, while the second scheme pertains to molecules whose oxygen atoms interact with an exchange cation or a hydroxyl group and one of the hydrogen atoms interacts with the oxygen atom of the lattice.

An analysis of the frequencies in the region of deformation vibrations allowed the determination of the valence angles α for each interaction scheme. In the analysis, the same principles and calculational formulas were employed as in the γ-Al_2O_3 investigation. It has been established that during D_2O adsorption the frequency of 1300 to 1315 cm^{-1} (1315 cm^{-1} for the natural form), which disappears at the dehydration temperature of 250°C, corresponds to scheme I. For 1315 cm^{-1}, the valence angle is 975° and for $m/M \to 1$, $(E_a - E_0)/(kT) = -0.613$.

It has been that found that the H_2O adsorption scheme II applies to the frequency of 1630 to 1640 cm^{-1}, which disappears at the dehydration temperature of 125°C. For 1635 cm^{-1}, the angle α is 1045° and for $m/M \to 1$, $(E_a - E_0)/(kT) \approx 0.0$.

Having determined the parameters $(E_a - E_0)/(kT)$ for water molecules adsorbed on different centers of various solids, we may derive the relations between the relative value of longitudinal relaxation times in NMR spectra in water and the solid phase-to-entire system mass ratio, which allow the calculation of structure characteristics of water for any mass of the solid phase in a liquid. The results of such work will be reported in the next communication.

NOTATION

M_e, molecular dipole moment; v_i, vibrational quantum numbers; Q_{i0}, zero vibration amplitudes; l_α, normalized vibrations; s, interatomic distance; m, mass of the solid phase; p_0, mass of a double adsorbed molecular layer; E_a, E_0, kinetic energies of nuclear vibrations of a H_2O molecule adsorbed on a solid surface and found in a liquid or vapor volume.

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