STRUCTURE OF WATER ADSORBED IN DISPERSE SYSTEMS WITH COMPLEX MINERALOGICAL COMPOSITION

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The existence of two kinds of complexes of adsorbed water molecules being coordinated around exchange cations or other active centers of the mineral crystal lattice surface is established in spectrum investigations of water interaction with clayey minerals with expanding crystalline lattice.

The change in density of adsorbed water as a function of its mass, the properties of the mineral surface, and the composition and concentration of cations detected in our experiments [1, 2] was the reason for formulating new investigations of the structure of the bound water. These investigations were based on the methods of vibrational spectroscopy, since, viz., these methods permits the most exact estimation of the configuration of different O_mH_n groupings including the configuration of the bound water, and their influence on the properties of the adsorbent.

The first stage of this research was concluded by obtaining and interpreting the IR spectra of the natural and Na forms of montmorillonite (Crimean kill) as a function of the mass of adsorbed water. The investigations were conducted on the basis of a UR-20 infrared spectrophotometer by using the vacuum system produced in a special vacuum cuvette. The vacuum apparatus assured a check on the vacuum and the vapor pressure of the adsorbate in the cuvette.

The construction of the vacuum cuvette permitted tracking the change in specimen weight in parallel with the scanning of the IR spectra. The specimen was displaced in the cuvette being used by using a screw mechanism rotated by a permanent magnet. The specimen was fastened in a frame from tantalum foil, suspended on the spiral of quartz balances having an autonomous reference scale. A microscope with a micrometer drum was used to read the weights.

The desorption of water by Crimean kill specimens was studied in the experiments. To do this, the predried finely ground powder was pressed into a tablet of 20 × 8 mm dimensions. The weight of the tablet fluctuated between 15-30 mg in different tests. The prepared tablets were dried and the weight of the dehydrated solid phase was determined. Then the process of their humidification under atmospheric conditions for 2-3 days was tracked, where specimens with a known initial humidity were set in the cuvette.

The process of removing the adsorbed water was realized because of heating the tablet by glowbar radiation with simultaneous evacuation, and a tubular detachable electric furnace was used to achieve low humidities.

Consequently, IR spectra were obtained for several specimens of hydrated natural and Na form montmorillonite.

The existence of a γ of frequencies in the domain of deformation vibrations of the water molecules, detected in the experiments, and the computations of these frequencies permitted an estimation of the degree of stability of the hydrogen bonds in the dehydration process. It was successfully shown that the 1633-cm^{-1} band occurring during the formation of two donor—acceptor (hydrogen) bonds in the plane of the H_2O molecule is most stable. Another orientation or another number of such bonds results in reduction of the adsorption energy of the water molecules. And this reduction, which characterizes the diminution in overlapping of the electron clouds between atoms interacting according to the hydrogen bond mechanism, is determined by the position of the maximum electron density in the space between the water molecule atoms.

The second stage in the spectroscopic investigation of clayey minerals was based on using the isotopic effect. Here D_2O was used as such isotopes of the water molecules.

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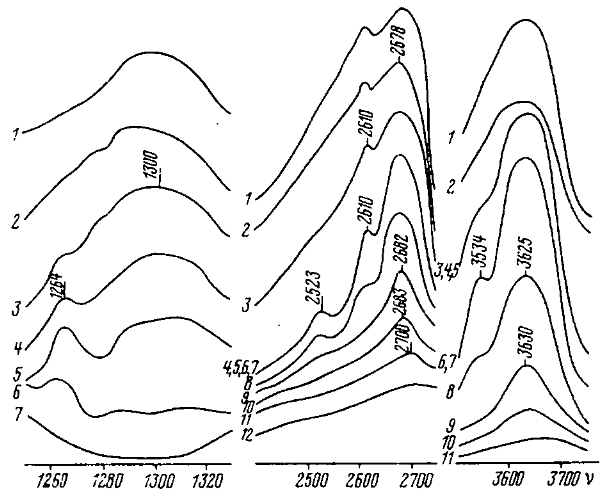


Fig. 1

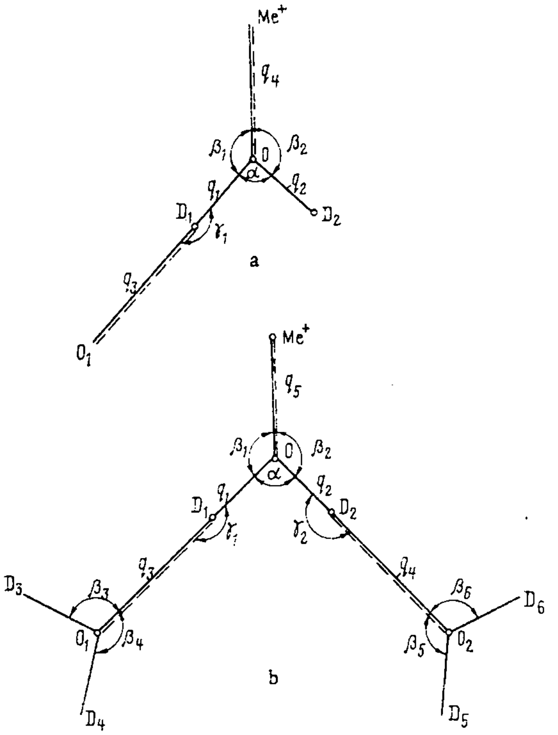


Fig. 2

Fig. 1. Change in the IR spectra of deuterated natural montmorillonite during desorption: 2) P = 12.9%; 3) 10.0; 4) 6.7; 5) 5.2; 6) 4.1; 7) 2.8; 8) 0.9; 9) 0%; 1) during sorption P = 8.1%. ν, cm^{-1}.

Fig. 2. Water molecule interaction with an exchange cation and an oxygen atom of the mineral surface (a) and with two oxygen atoms (b).

It is well known that the molecule properties dependent mainly on the electron structure remain constant during isotope substitution while the vibration frequencies, the band intensities in the vibrational spectra, the moments of inertia, the rotational frequencies, and other molecule properties dependent on the atom mass can vary substantially. This is especially characteristic for hydrogen because the relative change in its mass during isotope substitution is large.

The rotational and vibrational spectra of a system of isotopic molecules yield additional data needed to determine the geometric parameters of the molecules and the force constants. The isotopic effect exerts essential aid in the analysis of molecular spectra, particularly in the referral of vibrations observed in the frequencies to some normal vibration of the molecule.

We took into account all these singularities of isotope exchange.

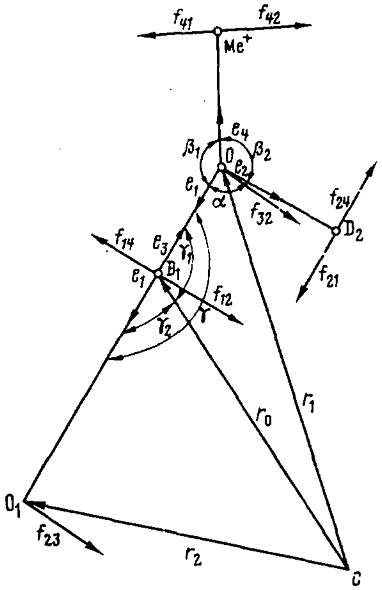
Changes in the IR spectra of the deuterated nature form of montmorillonite are shown in Fig. 1 for adsorption in the ranges of 1200-1300, 2500-2600, and 3500-3700 cm^{-1}.

It is known that the range 1200-1300 cm^{-1} corresponds to deformation vibrations of the D_2O molecules, and an analysis of the spectra obtained is started more conveniently with a computation of the frequencies of these vibrations. As is seen from Fig. 1, a broad band with the maximum of 1300 cm^{-1} corresponds to the greatest degree of hydration, while the bands 2680 and 2610 cm^{-1} correspond in the domain of valence vibrations.

As desorption proceeds, a comparatively narrow 1264-cm^{-1} band is extracted from the total contour of the deformation vibrations band, where the former vanishes for a low degree of humidity, to whose appearance the formation of the 2523-cm^{-1} band in the valence vibrations domain corresponds.

The frequencies of the deformation vibrations of the D_2O molecule for its different complexes are computed by means of the formula

$$\nu_{\alpha\alpha}^2 = D_{\alpha\alpha} + \sum_{\alpha\neq\mu} \frac{D_{\alpha\mu}D_{\mu\alpha}}{D_{\alpha\alpha}-D_{\mu\mu}} . \tag{1}$$



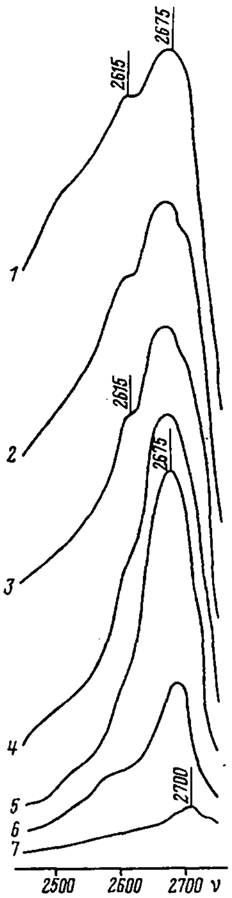


Fig. 3

Fig. 4

Fig. 3. Fragment of the scheme governing water molecule interaction with an exchange cation and an oxygen atom of the clayey mineral surface.

Fig. 4. Change in the IR spectra of the deuterated Na form of montmorillonite during desorption: 1) P = 8.5%; 2) 4.4; 3) 3.0; 4) 1.5; 5) 0. ν, cm^{-1}.

which El'yashevich [3] obtained by starting from the properties of the secular equation under the condition that $|D_{\alpha\mu}| \ll |D_{\alpha\alpha} - D_{\mu\mu}|$. The quantities $D_{\alpha\alpha}$, $D_{\alpha\mu}$, $D_{\mu\alpha}$, $D_{\mu\mu}$ are called total interaction coefficients. They are found as follows

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

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

The kinematic interaction coefficients for a number of coordinate pairs can easily be computed by means of equations presented in [3, 4].

However, an additional analysis is required to perform these computations when the angles $O_1 \ldots D-O$, equal to 180°, take part in the interaction, i.e., in the case of linear hydrogen bridges.

Let us examine the scheme *a* (Fig. 2) where the interaction coordinates of the D_2O molecule with an exchange cation and oxygen atom of the clayey material surface are indicated.

Let us form the matrix B [4], which expresses the natural vibrational coordinates in terms of displacement of the atoms from equilibrium. To do this we again isolate a fragment of the scheme mentioned, as is represented in Fig. 3.

According to [5], the rate of change of the angles O, D_1, O_1 is

$$\dot{\gamma}=\dot{\gamma}_1+\dot{\gamma}_2=-\left(\mathbf{f}_{32}\frac{1}{S_1}+\mathbf{f}_{23}\frac{1}{S_2}\right)\dot{\mathbf{r}}_0+\mathbf{f}_{32}\frac{1}{S_1}\dot{\mathbf{r}}_1+\mathbf{f}_{23}\frac{1}{S_2}\dot{\mathbf{r}}_2, \tag{3}$$

where $\dot{\mathbf{r}}_0$, $\dot{\mathbf{r}}_1$, $\dot{\mathbf{r}}_2$ are vectors describing the instantaneous position of the atoms O, D_1, O_1; S_1, S_2 are the instantaneous bond lengths, and $\mathbf{f}_{32}$, $\mathbf{f}_{23}$ are unit vectors drawn in the instantaneous plane of the valence angle perpendicular to the instantaneous directional vectors $\mathbf{e}_2$ and $\mathbf{e}_3$.

But as is seen from Fig. 3, $\mathbf{f}_{32} = \mathbf{f}_{23} = \mathbf{f}_{12}$. Then for the row elements of the matrix B corresponding to the natural coordinate of the change in angle formed by the atoms O, D_1, O_1 with the atom D_1 at the apex, we obtain, respectively,

$$-\frac{\mathbf{f}_{12}}{S_1};\quad -\frac{\mathbf{f}_{12}}{S_2};\quad \left(\frac{\mathbf{f}_{12}}{S_1}+\frac{\mathbf{f}_{12}}{S_2}\right).$$

Introducing the dimensionless constants $S_0/S_1 = G_1$ (S_0 is the equilibrium bond length in a methane molecule, equal to 1.09 Å) instead of the equilibrium distances, we finally obtain

$$-\mathbf{f}_{12}G_1;\quad -\mathbf{f}_{12}G_2;\quad \mathbf{f}_{12}(G_1+G_2).$$

The expression of the natural vibrational coordinates for water molecules interacting according to the scheme extracted, in terms of the displacement of atoms by using the matrix B, is written as follows:

$$\begin{array}{cccccc}
 & D_1 & D_2 & O & Ca & O_1 \\
q_1 & \mathbf{e}_1 & 0 & -\mathbf{e}_1 & 0 & 0 \\
q_2 & 0 & \mathbf{e}_2 & -\mathbf{e}_2 & 0 & 0 \\
q_3 & \mathbf{e}_1 & 0 & 0 & 0 & -\mathbf{e}_1 \\
q_4 & 0 & 0 & \mathbf{e}_4 & -\mathbf{e}_4 & 0 \\
\alpha & -\mathbf{f}_{12}G_1 & -\mathbf{f}_{21}G_1 & G_1(\mathbf{f}_{12}+\mathbf{f}_{21}) & 0 & 0 \\
\beta_1 & -\mathbf{f}_{14}G_1 & 0 & \mathbf{f}_{14}G_1+\mathbf{f}_{41}G_3 & -\mathbf{f}_{41}G_3 & 0 \\
\beta_2 & 0 & -\mathbf{f}_{24}G_1 & \mathbf{f}_{24}G_1+\mathbf{f}_{42}G_3 & -\mathbf{f}_{42}G_3 & 0 \\
\gamma & \mathbf{f}_{12}(G_1+G_2) & 0 & -\mathbf{f}_{12}G_1 & 0 & \mathbf{f}_{12}G_2
\end{array}$$

In order to obtain computational formulas for the matrix elements of the kinematic coefficients, let us perform the following operations. Let us select a row referring to the coordinates whose kinematic interaction must be determined in the matrix B, let us multiply the elements of these rows located in columns whose numbers agree with the numbers of the atoms which are common for the coordinate pairs selected term by term, and let us also multiply the products of the common atoms by ε_i and let us add the results ($\varepsilon_i = m_0/m_i$, where m_i is the mass of a common atom and m_0 is the spectroscopic mass of the hydrogen atom, $m_0 = 1.088$ atomic units).

The magnitude of the angles and the lengths of the chemical bonds must be known in order to determine the numerical values of the kinematic coefficients.

The natural coordinates for an isolated water molecule have been determined reliably and are $\alpha = 104°31$ $S_{OH} = 0.96$ Å, then $G_1 = 1.13$.

Taking the length of the hydrogen bridge R_{OO} 2.80 Å as the average observed in different crystal hydrates, we obtain $S_{H-O} = 1.84$ Å, then $G_2 = 0.59$. The spacing between the O—Ca atoms is 2.40 Å, then $G_3 = 0.45$.

One of the most important steps in the determination of the kinematic coefficients is the selection of the angles β_1, β_2, β_3, β_4 for the hydrogen bonds.

We examined a plane configuration for the arrangement of atom-acceptors of the electrons relative to the oxygen atom of the water molecule, and the values of the angles β_1 and β_2 were taken as 127.75°.

According to [6], the following values of the force constants were taken in the initial version of the computation: $K_{q_1,q_1} = 12.87 \cdot 10^6$ cm^{-2} for the interaction of a valence HOH bond with itself; $K_{\alpha\alpha} = 0.9113 \cdot 10^6$ cm^{-2}

for the HOH valence angle with itself; $K_{q_1q_2} = -0.1271\cdot 10^6\ \mathrm{cm}^{-2}$ for the two valence bonds; $K_{\alpha q_1} = -0.168\cdot 10^6\ \mathrm{cm}^{-2}$ for a valence angle with a valence bond; $K_{\beta\beta} = K_{\gamma\gamma} = 0.05\cdot 10^6\ \mathrm{cm}^{-2}$ for the angle of a hydrogen bond with itself; $K_{\alpha\gamma} = K_{\alpha\beta} = 0.005\cdot 10^6\ \mathrm{cm}^{-2}$ the interaction of any angles having two or one common atoms; $K_{q_3q_3} = 0.22\cdot 10^6\ \mathrm{cm}^{-2}$ for a hydrogen bond with itself; $K_{q_1\beta} = 0.01\cdot 10^6\ \mathrm{cm}^{-2}$ for a valence bond with an angle for a hydrogen bond; $K_{\alpha q_3} = 0.003\cdot 10^6\ \mathrm{cm}^{-2}$ for a valence angle with a hydrogen bond, and $K_{q_1q_3} = -0.002\cdot 10^6\ \mathrm{cm}^{-2}$ for a valence with a hydrogen bond.

Computation of the nonsymmetric complex (Fig. 2a) for these same force constants determined the frequency at 1250 cm^{-1}.

However, it must be noted that in selecting the force constants, their probabilistic mean values governing the energy of the hydrogen bond to some degree were taken, and the magnitude taken for the force constant of the hydrogen bond itself $0.22\cdot 10^6\ \mathrm{cm}^{-2}$ corresponds to its energy of 5 kcal/mole.

At the same time, the differential heat of water adsorption by Ca-montmorillonite [7] observed in experiments, and by hydrated surfaces of a number of oxides TiO_2, SiO_2 [8] for small surface populations, is almost 20 kcal/mole. Such a rise in the adsorption energy is ordinarily explained by the interaction of a water molecule with exchange cations or coordination-unsaturated Si, Al atoms of the crystal lattices. According to [6], the force constant $0.9\cdot 10^6\ \mathrm{cm}^{-2}$ and the force constant of the angles in the bond (according to Fig. 2a these angles are β_1, β_2) $0.06\cdot 10^6\ \mathrm{cm}^{-2}$ correspond to this binding energy. The computations performed for the frequency of the deformation vibrations of the D_2O molecule in a nonsymmetric complex with new force constants determined it to be 1262 cm^{-1}, which is near that detected in experiments.

As is seen from Fig. 1, only the frequency 1300 cm^{-1}, specifying the existence of associates of the water molecules which are coordinated around the exchange cations or other active surface centers, is detected in the first period of dehydration of the natural form of montmorillonite (a change in the humidity from 13 to 10%) in the IR spectra 1, 2, 3 in the deformation vibrations region.

The interaction diagram of an adsorbed D_2O molecule and an exchange cation, a hydroxyl OD group, and the generator of hydrogen bonds with the adjacent water molecules are shown in Fig. 2b.

A computation of the D_2O deformation vibrations frequency in such a symmetric complex for force constants corresponding to the hydrogen bond energy 5 kcal/mole determined it to be 1300 cm^{-1} and such a result corresponds exactly to that detected in experiments.

Let us turn to the frequencies observed in the domain of valence vibrations of the water molecule. As is seen from Fig. 1, two frequencies, 2680 and 2610 cm^{-1}, are detected in the 2500-2700 cm^{-1} domain in the spectra 1, 2, 3 in the initial dehydration period (humidity change from 13 to 10%). It is logical to assume that these frequencies determine the vibrations of the OD group of the isotopic water molecule in symmetric complexes since of these spectra only one frequency, 1300 cm^{-1}, appear in the deformation vibration domain.

The frequencies of the valence vibrations can be computed by means of (1) under the condition that the nondiagonal total interaction coefficients are small in absolute value as compared with the difference between the values of the diagonal elements (the total interaction coefficients).

It is easy to show that the contribution to the valence vibrations frequency from a combination of elements $D_{\lambda\mu}D_{\mu\lambda}/D_{\lambda\mu} - D_{\mu\mu}$ in (1) is negligible for the total interaction coefficients $D_{q_3q_3}$, $D_{q_4q_4}$, $D_{q_5q_5}$, $D_{\alpha\alpha}$, $D_{\gamma\gamma}$, $D_{\beta\beta}$.

But $D_{q_1q_1} = D_{q_2q_2}$ in a symmetric complex (see Fig. 2b), then the solution (1) acquires the simple form

$$\nu_s^2 = D_{q_1q_1} - D_{q_1q_2}, \quad \nu_{us}^2 = D_{q_1q_1} + D_{q_1q_2}, \qquad (4)$$

where ν_s is the frequency of the symmetric and ν_{us} of the nonsymmetric vibrations.

By varying several values of the diagonal and nondiagonal force constants for the frequencies found in the experiment, exact values of these constants can be determined from (4). Thus, it turns out to equal $12.11\cdot 10^6\ \mathrm{cm}^{-2}$ for a D_2O molecule adsorbed in a symmetric complex by the natural form of montmorillonite, while the nondiagonal force constant is $K_{q_1q_2} = 0.06\cdot 10^6\ \mathrm{cm}^{-2}$.

The appearance of the third maximum 2520 cm^{-1} in the spectra 4-9 in the 2500-2700-cm^{-1} band and the second maximum in the spectra 3-8 in the 3500-3700-cm^{-1} band (Fig. 1) as the humidity changes from 7 to 0% can be given a foundation by the existence of nonsymmetric complexes, i.e., by the interaction of a water molecule with an exchange cation, particularly the Ca cation, and an oxygen atom of the clayey mineral surface.

It is well known that the adsorption of exchange cations in montmorillonite occurs mainly in negative uncompensated charges of the structural cell, formed because of replacement of the trivalent aluminum by ions of lower valency, usually magnesium in octahedral grids. The divalent Ca^{+2} cation interacts at once with two negative charges located on opposite sides of the silicate layers coupling the single water molecules with the vacancies of the tetrahedral grids. According to [9], the bases for hollows in the tetrahedral grids have a different geometric shape in different cases: a triangle with side $2l$, a ditrigon and a hexagon with side l'. Taking $l = l' = 2.65$ Å in a first approximation (the usual O—O spacing in S_i tetrahedra) and disposing the exchange cation and its bound water molecule in this geometric space, we easily see the impossibility of the formation of symmetric complexes.

It should be noted that the formation of a second maximum in the spectra 4, 5, 6 in the deformation vibrations domain (the 1264-cm^{-1} band), which governs the frequency of the deformation vibrations of the D_2O molecule in nonsymmetric complexes, as has already been shown, corresponds to the origination of the frequencies 2523 and 3534 cm^{-1}.

The force constants of the OD bonds can also be computed by using (1), but as an analysis showed, the difference in the quantities $| D_{q_1q_1} - D_{q_2q_2} |$ turned out to be close to $| D_{q_1q_2} D_{q_2q_1} |$, in absolute magnitude and, hence, in this case the frequencies and force constants were determined on the basis of the solution of the simple secular equation

$$\begin{vmatrix} D_{q_1q_1} - \nu^2 & D_{q_1q_2} \\ D_{q_2q_1} & D_{q_2q_2} - \nu^2 \end{vmatrix} = 0 \tag{5}$$

with the contribution of the diagonal and nondiagonal total interaction coefficients of the other bonds neglected.

Formulas to compute the counterphase ν_{uf} and cophasal ν_{sf} vibrations frequencies of the OD bonds in a nonsymmetric complex obtained from (6)* are the following:

$$\nu_{uf} = \left\{ \frac{1}{2} (D_{q_1q_1} + D_{q_2q_2}) + \frac{1}{2} [(D_{q_1q_1} + D_{q_2q_2})^2 - 4 (D_{q_1q_1}D_{q_2q_2} - D_{q_1q_2}D_{q_2q_1})]^{1/2} \right\}^{1/2}, \tag{6}$$

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

where

$$\begin{aligned} D_{q_1q_1} &= A_{q_1q_1}K_{q_1q_1} + A_{q_1q_1}K_{q_2q_1} + A_{q_1\alpha}K_{\alpha q_1}; \\ D_{q_1q_2} &= A_{q_1q_1}K_{q_1q_2} + A_{q_1q_2}K_{q_2q_2} + A_{q_1\alpha}K_{\alpha q_1}; \\ D_{q_2q_1} &= A_{q_2q_1}K_{q_1q_1} + A_{q_2q_2}K_{q_2q_1} + A_{q_2\alpha}K_{\alpha q_2}; \\ D_{q_2q_2} &= A_{q_2q_1}K_{q_1q_2} + A_{q_2q_2}K_{q_2q_2} + A_{q_2\alpha}K_{\alpha q_2}. \end{aligned}$$

Products of the force constants by the kinematic bond coefficients, which yield a slight correction, were not taken into account in determining the total interaction coefficients.

Values of these constants were found for the frequencies found in experiment by variating several values of the diagonal and nondiagonal force constants. Thus, $K_{OD_1} = 11.1 \cdot 10^6$ cm^{-2}, $K_{OD_2} = 11.68 \cdot 10^6$ cm^{-2} for a D_2O molecule adsorbed by the natural form of montmorillonite.

It is well known that replacement of hydrogen by deuterium occurs in the hydroxyl groups of the surface and in the hydroxyl groups located on the side faces in the montmorillonite, in addition to the formation of heavy-water complexes during isotopic exchange. It should be assumed that the 2680-cm^{-1} band refers to the hydroxyl groups of such faces, and the 3625-cm^{-1} band to the OH groups of the octahedral grids of the silicate layers.

As is seen from Fig. 1, a second maximum (the 3530-cm^{-1} band) occurs in the 3500-3700-cm^{-1} range in the spectra 4-9. Its formation is due to the appearance of a nonsymmetric complex in the vibrations spectra. It can therefore be considered that the exchange of deuterium by hydrogen (as computations showed) in the free OD bond of the water molecule interacting with an exchange cation and an oxygen atom of the tetrahedral grid occurs within the tetrahedral vacancies under the influence of a high vacuum and temperature. In fact, by substituting the value of the coefficient $A_{q_2q_2}$ for the OH bond, which equals 1.068, and for the force constants

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*As in Russian original – Publisher.

$11.68 \cdot 10^6$ cm^{-2} calculated earlier into (6), the value of the counterphase frequency $\nu_{uf} = 3530$ cm^{-1} was obtained.

Changes in the IR spectra of the deuterated Na form of montmorillonite during dehydration are represented in Fig. 4.

Because of strong absorption of infrared radiation by the solid phase skeleton, the spectra of the deformation vibrations of the water molecule were not obtained successfully in the 1200-1300-cm^{-1} range. At the same time, only two maxima, 2675 andd 2620 cm^{-1}, specifying the existence of adsorbed water molecules in symmetric complexes as for the natural form, are detected in the 2500-2700-cm^{-1} band in practically the whole range of humidities. Their values are established by computing the force constants by means of (4):

$$K_{q_1q_1} = K_{q_2q_2} = 12.13 \cdot 10^6 \text{cm}^{-2}, \ K_{q_1q_2} = 0.12 \cdot 10^6 \text{cm}^{-2}.$$

As is seen from Fig. 4, there are no bands governing the existence of adsorbed water molecules in nonsymmetric complexes in spectra in the 2500-2700-cm^{-1} and 3500-3700-cm^{-1} bands. And this circumstances is due to the peculiarities of fastening the ions in the interlayered space. The Na$^+$ cation interacts just with one negative charge of the structural cell and does not bind the water molecule in the tetrahedral vacancy but remains in the monolayer of the interpacket space.

However, for a very low adsorbed water content, the presence of its closed molecules is always observed at the tetrahedral vacancies, as is confirmed by the presence of weakly expressed bands with a 2600-cm^{-1} frequency in the spectra 5, 6 (Fig. 4).

A shift in the main bands in the valence vibrations ranges of the OD groups to the high-frequency side to 2700 cm^{-1} is observed in the spectra 10-12 (Fig. 1) and spectrum 7 (Fig. 4) upon total dehydration of the mineral surface. Such a shift, due to the unloading of the hydroxyl groups from the water molecules, is determined by a 1.5% increase in the force constants of the OD bonds, and in conformity with [5], a 0.5% linear deformation of the bond, which confirms the deduction about the presence of deformations in a crystal lattice under the influence of adsorbed water, estimated on the basis of diffractometer measurements.

Thus, the experimental spectrum investigations performed for water interaction with clayey minerals with an expanding crystal lattice during dehydration, and the computation of the deformation vibrations frequencies and force constants of the valence bonds of the water molecules, permitted execution of still another step in a study of the mechanism of the water structure formation on the solid phase surface of disperse systems.

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