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V. I. Kvlividze

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V. I. Kvlividze

NUCLEAR MAGNETIC RESONANCE OF PROTONS AT 93°K IN WATER ADSORBED ON SILICA GEL

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Previously ([1]) we studied nuclear magnetic resonance (NMR) signals from the protons of the hydroxyl groups of silica gel and of adsorbed water at different surface coverages at room temperature. It is of interest to continue these investigations in the low-temperature region, since this will make it possible to obtain more detailed information on the structure of the hydroxyl coating and on the state of water on the adsorbent surface. In this work we studied coarse-porous silica gel KSK-3 with a specific surface area of 340 m^2/g, whose adsorption properties were studied in ([2]). The silica gel was previously pumped out at a temperature of 200°C to a vacuum of 10^{-5} mm Hg. The degree of hydration of the surface after this treatment was 4.3 μmol/m^2 H_2O, or 8.6 μmol/m^2 OH. The dosing of water into the ampoules used to obtain the NMR spectra was carried out in the same way as in ([1]). To improve heat exchange between the adsorbent and the walls of the ampoules, the latter were filled with helium at a pressure close to atmospheric. In this case, as shown in ([3]), desorption of water vapor does not occur upon rapid cooling of the ampoule. The absorption signals of NMR were measured on an NMR spectrometer for broad lines ([1]). The coil of the high-frequency generator was wound on a glass frame with bare copper wire in order to eliminate parasitic signals from the protons of the insulation, and was placed in a cryostat that made it possible to maintain the temperature with an accuracy of $\pm 0.5^\circ$ in the range from 83 to 273°K. To measure the second moments, the NMR spectra were recorded with a modulation amplitude $H_m = 0.75$ oersted, which led to distortion of the central narrow component of the signal. To determine the true line shape and the width of the narrow component, signals were recorded at values $H_m = 0.23,\ 0.13$, and 0.08 oersted. Since in almost all cases both a broad and a narrow component were observed simultaneously, the gradual decrease of H_m made it possible to find the undistorted signal shape. Figure 1 shows NMR signals from samples with different water contents (a). The results of processing the spectra are given in Table 1.

Table 1

Sample no.	P/P at room temperature	Amount of adsorbed water, mmol/g	Amount of adsorbed water, μmol/m^2	Second moment, Oe^2	Width of the broad component, Oe
1	0	0	0	2.0 ± 0.2	
2	0.1	0.75	2.2	12.2 ± 1.0	8.8 ± 0.5
3	0.53	2.75	8.1	23.0 ± 1.0	11.0 ± 0.4
4	0.74	7.0	20.6	23.5 ± 1.0	12.0 ± 0.4
5	0.83	12.5	37.0	29.7 ± 1.5	13.9 ± 0.4
6	0.89	19.5	57.0	30.1 ± 1.5	14.1 ± 0.4
7	0.96	44.0	130.0	31.1 ± 1.5	14.2 ± 0.4

Let us consider the line shape of the proton signal from the initial silica-gel sample–sample 1 ($a = 0$). The line width at a temperature of 93°K is equal to the line width at room temperature ([1]), which agrees with the data of O' Reilly ([4]). Owing to the higher signal-to-noise ratio at low temperatures than at room temperature, we were able to investigate in more detail the form of the absorption line of the hydroxyl coating. The analysis shows that the line consists of three Gaussian components, the second moments (S) co-

which are respectively equal to 0.06, 0.7, and 3.8 oersted^2, indicating the presence on the silica-gel surface of silanol sites of at least three different types. It is of interest to carry out calculations of the second moment of the NMR line by the Van Vleck formula ([5]). In doing so we took into account that the value of S is determined mainly by the nearest environment of the nuclei under study. The latter, with a known degree of approximation, makes it possible to apply schemes for the structure of crystalline modifications of silica ([6]) to amorphous silica gel, since the basic structural parameters needed for calculating S change only slightly in this case (see, for example, ([7])). Comparison of the calculated values of the second moments with the experimentally obtained S_{exp} makes it possible to assume the existence of the following possible types of silanol sites:

1. Isolated OH groups, whose nearest neighbors are at a distance of $5.4 \div 5.2$ Å ($S_{\text{theor}} = 0.05 \div 0.075$ oersted^2, $S_{\text{exp}} = 0.06$ oersted^2). At greater distances between protons, S_{theor} becomes considerably smaller than the experimental value of the second moment. These groups constitute $\sim 25\%$ of the surface hydroxyls.

2. Isolated paired OH groups, belonging either to one and the same or to neighboring Si atoms, with a distance between protons of $2.52 \div 2.6$ Å ($S_{\text{theor}} = 0.6 \div 0.72$ oersted^2, $S_{\text{exp}} = 0.7$ oersted^2). These groups contain $\sim 30\%$ of the protons of the hydroxyl groups.

Fig. 1. Derivatives of the NMR absorption signals of protons at a temperature of 93° K. 1 –sample 1, 2 –sample 2, 3 –sample 3, 4 –sample 4, 5 –sample 7. Components are indicated by dotted lines.

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3. OH groups having two, three, or four neighbors at distances of $2.52 \div 2.6$ Å ($S_{\text{theor}} = 2.9 \div 4.6$ oersted^2, $S_{\text{exp}} = 3.8$ oersted^2). The number of protons in these groups is $\sim 45\%$. According to infrared-spectroscopy data ([8]), at a high concentration of OH groups on the surface, some of them may be linked by hydrogen bonding. However, the latter will not have a substantial effect on the magnitude of the second moment of the NMR signal.

Silica-gel samples containing adsorbed water give a complex signal (see Fig. 1), which in a first approximation may be regarded as consisting of two lines—a narrow and a broad one. The width of the narrow component for all samples with adsorbed water is 0.5 ± 0.05 oersted and coincides with the line width of sample 1. With increasing adsorption, the intensity of this component decreases and, for example, for sample 7 amounts to less than 0.15% of the total signal intensity. As is known ([9]), the NMR line width and second moment depend both on the arrangement of the resonating nuclei and on their mobility. The narrow component of the signal in our samples may be associated either with mobile water molecules or with OH groups. For an immobile isolated water molecule, if the interproton distance is taken as 1.54 Å, the second moment is equal to 27 oersted^2, which is considerably higher than the experimental value for the narrow component. Only water molecules undergoing both translational and rotational motion simultaneously can give the observed narrow line. The existence of such mobility is unlikely at so low a temperature. The opposi-

The fact that the intensity of the narrow component decreases with increasing adsorption while the line width remains unchanged also argues against associating the narrow component with mobile water molecules. If the presence of mobile water molecules is assumed, then, with increasing adsorption in the region of low coverages, the intensity of the narrow component should have increased, since the binding energy of the molecules to the surface, according to data on the differential heats of adsorption ([2]), decreases with increasing a, and the number of mobile molecules should grow. It is precisely this type of change in the signal that we previously observed at room temperature ([1]), when the signal was due to mobile molecules. Thus, the narrow component is unlikely to be associated with mobile water molecules. The observed behavior of the narrow signal can be explained by the presence, on the silica-gel surface, of hydroxyls at which water adsorption does not occur at this coverage. From the width of the signal it may be concluded that these hydroxyls are those of the first two types.

A small contribution to the narrow component is made by protons located in the glass of the ampoule and in the glass framework of the coil.

The broad component of the signal is due to the protons of water and to hydroxyl groups near which molecules of adsorbed water are located. With increasing adsorption the signal intensity increases and the second moment increases (see Table 1). Comparison of the NMR signals of sample 1 and sample 2 ($a = 2.2\,\mu\text{mol/m}^2$) shows that the signal from silanol sites of the first and second types changes practically not at all. At the same time, the component corresponding to silanol sites of the third type undergoes a noticeable change. This indicates the absence of interaction of water molecules with silanol sites of the first two types. Single and paired OH groups are not the principal adsorption centers in this range of coverages. This is in agreement with earlier infrared-spectral studies ([8]), according to which the band of the fundamental stretching vibrations of OH groups undergoes no changes in the initial region of adsorption.

The change in the NMR spectrum from OH groups of the third type indicates that water molecules are adsorbed preferentially at sites with the highest density of hydroxyl groups. An estimate of the intensity of the NMR signal components shows that, on the average, in sample 2 there is ~ 1 OH group per adsorbed water molecule; i.e., water molecules are adsorbed in clusters around the most active centers. As indicated earlier ([1,2]), the differential heats of adsorption of water vapor in this region are rather large (18–13 kcal/mole) and, as has been noted, can hardly be explained solely by the formation of hydrogen bonds. It must be assumed that, in the initial region of adsorption, water molecules are adsorbed at more active centers, the number of which is small. The assumption of centers of a second kind on the basis of infrared spectra was previously put forward by Sidorov ([8]). As indicated ([2]), such centers may be coordinatively unsaturated silicon atoms on the surface of silica gel, capable of forming a donor-acceptor bond between their free *d*-orbitals and the lone pair of electrons of the oxygen of the water molecule ([10]). In interaction through a coordination bond, the water molecule will be adsorbed on the most coordinatively unsaturated silicon atoms, containing the maximum number of OH groups, which agrees well with our data on the greatest activity of surface sites with the maximum concentration of OH groups and does not contradict adsorption measurements that establish a relation between the degree of hydration and the specific adsorption capacity of the surface ([11]). The water molecules will then be surrounded by 3–4 hydroxyl groups. In this case, along with coordination bonds, some of the molecules will form hydrogen bonds both with surface O and H atoms and with one another, creating isolated islands. Calculation of the second moment for such a model gives a value close to the experimental value S for sample 2. Pri-

the approximate nature of the calculation does not make it possible to choose unambiguously a model for the arrangement of water molecules on the surface.

From the data on the number of type-III OH groups, the data from the NMR spectra at room temperature, and also the data on the number of OH groups participating in adsorption, one can estimate the number of primary adsorption

centers, which in all cases proved to be no more than $3 \cdot 10^{17}$ centers per 1 m^2.

For sample 3, on which an amount of water corresponding to a Brunauer monolayer was adsorbed, the second moment is 23 ± 1 Oe^2. For idealized models considering a monolayer arrangement of water molecules relative to the surface, the theoretically calculated value of S proves to be less than 20 Oe^2. For structures 2–3 molecules thick, S increases to 22–23 Oe^2, which is close to the experimental value for sample 3. For sample 4 the second moment differs little from the value of S for sample 3 (see Table 1). Apparently, in sample 3 we have islands of adsorbed molecules 2–3 water molecules thick, while in sample 4 these islands grow along the surface without a substantial increase in their thickness.

For samples 5, 6, and 7 the experimental values of S are respectively 29.7 ± 1.5, 30.1 ± 1.5, and 31.1 ± 1.5 Oe^2. The increase in S is associated with the formation of polymolecular structures (number of layers greater than 5). Let us compare the second moment for frozen water in silica gel with the second moment for ice (36.7 ± 1.7 Oe^2) [12]. The different values of S for ice and for water in silica gel at high fillings can be explained by a difference between the structure of the frozen adsorbed water and that of normal ice, as well as by the high dispersion of the frozen water in the capillaries of the silica gel, when the contribution of surface protons to the value of S is large. The influence of surface water molecules can be estimated by calculating the second moment of the NMR signals of water in samples 5, 6, and 7 under the assumption that, with the corresponding weight, it will be composed of the values of S for the hydroxyl groups of the silica-gel surface, the first layer of adsorbed molecules, and water molecules in the bulk. The corresponding second moments are 2.0, 27, and 36.7 Oe^2. The values of S obtained by this calculation for these samples, with a seating area of the water molecule of 21 $Å^2$, proved to be 31, 32.5, and 34.5 Oe^2. As can be seen, the values S_{theor} are obtained larger than the experimental ones, and the discrepancy increases as the amount of adsorbed water increases. Thus, allowing for the contribution of surface protons to the value of S does not completely explain the decrease of the second moment. This is apparently connected with the fact that the frozen adsorbed water is less dense than ice [3], and the value of S for molecules in the bulk is less than 36.7 Oe^2. Studies of the temperature dependence of the second moment and of the line shape of the NMR signals for these samples, which are being carried out in our laboratory, will bring greater clarity to this question.

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Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.