THE POSITION OF HYDROGEN ATOMS IN NATROLITE

S. P. Gabuda, A. G. Lundin, G. M. Mikhailov, and K. S. Aleksandrov

Institute of Physics, Siberian Division of the Academy of Sciences, USSR;
Siberian Technological Institute
Translated from Kristallografiya, Vol. 8, No. 3,
pp. 388-392, May-June, 1963
Original article submitted March 29, 1962

We have used the method of proton magnetic resonance to study a natural single crystal of natrolite at room temperature. We have found the relationship between the proton magnetic resonance spectra and the orientation of the crystal in an external magnetic field. We have found that water molecules in natrolite at room temperature occupy a fixed position in the structure and that there are four different proton-proton directions in the crystal. The distances between the protons in H_2O molecules is r = (1.59 ± 0.015)A. We have used the ideas of crystal chemistry to calculate the coordinates of the protons in the natrolite structure.

Natrolite, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, is one of the representatives of a large group of minerals—zeolites. Although the adsorption properties of zeolites have long been known, until the present there has been little information on the state of the adsorbed molecules or the form of their connection with the zeolite framework. This is mainly due to the difficulty in determining the positions of the protons by x-ray structural analysis. Methods should therefore be used which are sensitive to hydrogen, in particular, the method of nuclear magnetic resonance [1], used in the present work.

The structure of natrolite was studied by x-ray diffraction methods in [2, 3], in which the positions of all atoms except the hydrogen atoms were determined. It was shown that the unit cell contains eight "formula units" of $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, i.e., 16 H_2O molecules. The space group of natrolite is C_{2V}^{19}; of 16 water molecules only four are therefore nonequivalent, all the H_2O molecules having an identical environment at the centers of irregular tetrahedra formed by two Na atoms and two oxygen atoms of the group $(Al, Si)O_4$.

We studied a specimen of natrolite (Khibiny) in the form of a colorless crystal with good faces measuring $10 \cdot 10 \cdot 16$ mm. The normals to the predominating faces of the crystal $\{110\}$ and $\{1\bar{1}0\}$ were taken to be the directions of the X and Y axes, and the Z axis was made to coincide with the [001] direction. With these coordinates the angle between the X and Y axes (according to [2]) was 91°. The previously described apparatus [4] was used to take the spectra of proton magnetic resonance for various orientations of the crystal relative to the external magnetic field H_0. The H_0 direction was rotated about the X and Z axes of the crystal (Fig. 1).

Theoretically, with the presence of comparatively isolated pairs of protons in the crystal the spectrum should be a doublet with a distance between the components described by the Pake equation [5, 1],

$$\Delta H = 3\mu r^{-3} \left[3 \cos^2 \delta \cos^2 (\varphi - \varphi_0) - 1 \right],$$

where ΔH is the distance between the components of the doublet, μ is the magnetic moment of the proton, $\underline{r}$ is the distance between protons in a proton-proton pair, δ is the angle of inclination of the interproton p—p vector
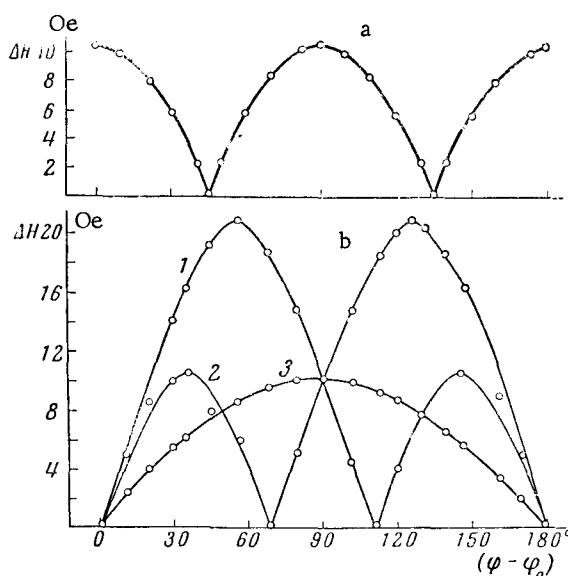

Fig. 1. Dependence of doublet splitting of proton resonance on the orientation of the crystal in a magnetic field. a) On rotation of the magnetic field about the Z axis; b) on rotation of the magnetic field about the X axis.

to the plane of rotation of the crystal, and φ_0 is the angle between the projections of the p–p vector onto the plane of rotation of the crystal and any of the axes in the crystal. By measuring ΔH as a function of φ we can use the Pake equation to determine r, δ, φ_0, i.e., the distance between the protons and the direction of the p–p vector. When there are several different directions of the p–p vectors the spectrum will consist of several doublets superimposed on one another.

Analysis shows that when the magnetic field rotates about the Z axis (Fig. 1a) the experimental relationship is described by the Pake equation when r = 1.590 ± 0.015 A, δ = 35°20' and φ_0 = 0, 90,180, 270° (the angles δ are measured from the XY plane, φ from the X direction). On the other hand, the spectra recorded during rotation of the field H_0 about the X axis (Fig. 1b) enable us to determine the number of nonequivalent p–p vectors in the structure. Curves 1 and 2 correspond to two p–p vectors lying in the plane of rotation of the crystal YZ at an angle of 70° to one another (φ_0 = 35° and 145°, δ = 0; the angles are measured from the Z direction, δ from the YZ plane). Curve 3 corresponds to a p–p vector lying in the XZ plane and having the direction φ_0 = 0, δ = ± 55°. Since it is known [2] that the Z (c) axis is a twofold screw axis, both values of the angle δ should exist, i.e., in the XZ plane there should also be two p–p vectors. This assumption is supported by the fact that the intensities of peaks corresponding to curve 3 are twice as high as those of the peaks corresponding to curves 1 and 2.

From the spectra of proton magnetic resonance it can therefore be concluded that in natrolite there are only four different proton-proton directions, that the distances between the protons are r = 1.59 ± 0.015 A and that the proton-proton vectors have the directions δ = 35 ±2°; φ_0 = 0, 90, 180 and 270°. Figure 2 is a schematic representation of the arrangement of p–p vectors in natrolite with respect to the principal axes.
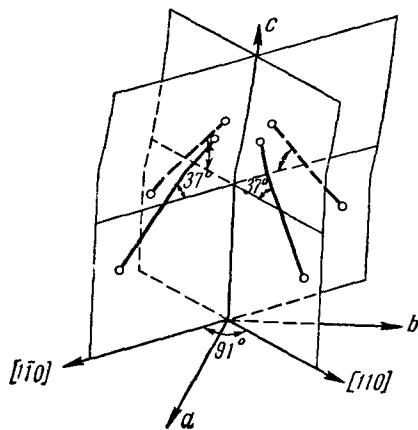

Fig. 2. Orientation of proton-proton directions in natrolite with respect to the principal axes.

As mentioned, the angle between the X and Y axes is 91°. It follows from the symmetry of the crystal that p–p vectors should lie in these planes, i.e., the angles should be 0, 91, 180 and 271°. This means that the curve in Fig. 1a should actually be two identical curves displaced relative to one another through 1°. However, this displacement is not noticeable experimentally, because of the considerable broadening of the peaks themselves due to intermolecular interaction.

In principle, a knowledge of interatomic distances and the directions of the p–p vectors still does not enable us to determine the coordinates of protons; however, in cases where the position of the heavy atoms is known, as in the case of natrolite, we can use crystal chemistry ideas to relate protons to a known structure [6, 7].

According to the accepted ideas of Bernal and Fowler [8], a molecule has four tetrahedral valences of approximately equal strength ($\sim \frac{1}{2}$ unit); two of these valences are positive and two are negative. Since the nearest environment of a water molecule in natrolite also has a tetrahedral configuration, it is natural to assume that the water molecule is oriented so that the positive valences are "locked" onto the electronegative oxygen atoms (hydrogen bonds are set up: $O-H\ldots O_{II}$; $O-H\ldots O_{III}$) [9], and the negative valences are bound to the electropositive Na atoms. Using this assumption and data on the interproton distance and the direction of the p–p vectors, we calculated the coordinates of protons in the natrolite structure; these coordinates are given in the table. Using the results of numerous determinations [10], we took the O–H distance in the water molecule to be 1.00 A. Figure 3a shows the arrangement of protons in natrolite with respect to the nearest neighbors of the molecule in the projection onto the ab plane.

It is an interesting fact that within the limits of experimental error the protons lie in the plane of three oxygen atoms $O_{II}-O_{III}-O_{H_2O}$. In fact, the angle of inclination of the p–p vector to the ab plane is 35 ± 2°, whereas the angle of inclination to the same plane for the $O_{II}-O_{III}$ direction, calculated from the structure [2], is 37°. This difference is within the limits of experimental error. On the other hand, the angle between the directions $O_{II}-O_{III}$ and Na–Na in a tetrahedron surrounding the water molecule is 77°, and not 90° as in a regular tetrahedron [2]. If the interactions of the positive valences of the H_2O molecule with oxygen O_{II}, O_{III} and negative valences with Na were the same, the difference of 13° would have to be divided equally and the

Coordinates of Protons in Natrolite

Atom	Position	x	y	z
16 H I	b	0.118	0.182	0.198
16 H II	b	0.069	0.134	0.051

protons would have to be displaced from the $O_{II}-O_{III}$ $-O_{H_2O}$ plane by $6.5°$.

In actual fact this angle is smaller, which points to the predominating effect of the hydrogen bonds $O-H \ldots O_{II}$ and $O-H \ldots O_{III}$ on the orientation of the water molecule in the natrolite structure (Fig. 3b). The angles of these hydrogen bonds are approximately the same and equal to $150°$ (Fig. 4).

In conclusion we should mention that the establishing of "immobility" of the H_2O molecule in the natro-
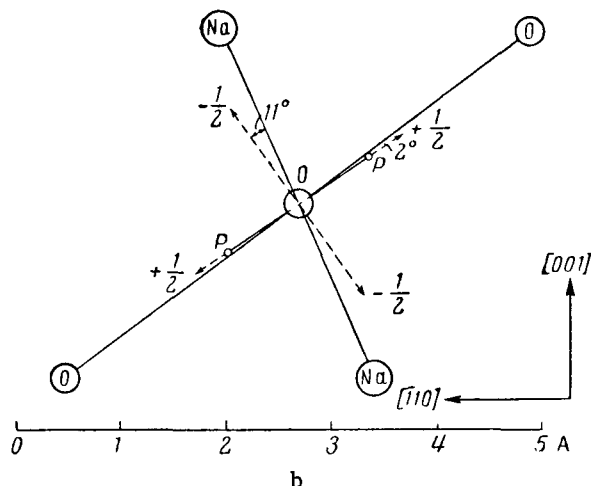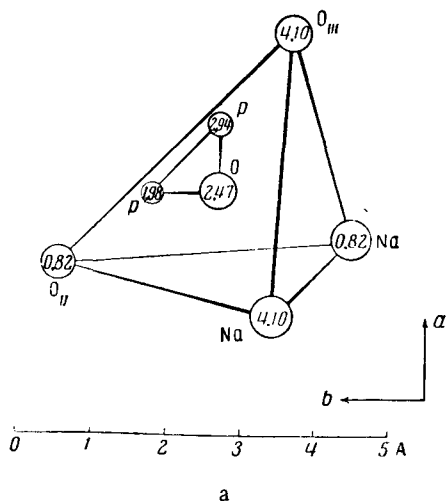

a

b

Fig. 3. Arrangement of protons in natrolite. Only the nearest environment of the H_2O molecule is shown. a) Projection onto the ab plane; b) projection onto the $\{110\}$ plane.
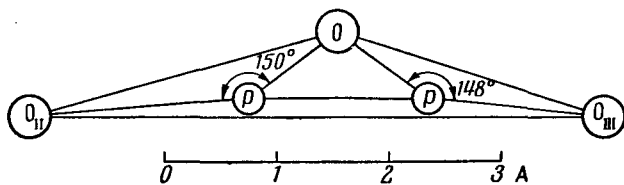

Fig. 4. Hydrogen bond in natrolite. The position of the protons is shown in the plane of three oxygen atoms.

lite structure is somewhat unexpected, since it is usually assumed that "zeolitic" water should have a certain degree of mobility in the channels of the zeolite structure. In fact, in some zeolites, for example in chabazite [11] and desmine [12], investigations by the nuclear magnetic resonance method show that at room temperature the water molecules are in a state of intense motion (reorientation). On the other hand, in some crystallohydrates, for example in potassium ferrocyanide [13] and in some hydrates of calcium and strontium halides [14], the water molecules are also fairly mobile at very low temperatures. We can therefore conclude that high mobility is not a characteristic feature of zeolitic water.

The absence of mobility of water molecules in natrolite at room temperature points to the predominance of the bond energy of the water molecules over the vibrational energy of these molecules. With increase in temperature the energy of molecular vibrations increases, and in the final analysis this leads to a comparatively easy liberation of the water molecule and its removal along the structure channels of natrolite.

LITERATURE CITED

1. E. Andrew, Nuclear Magnetic Resonance [Russian translation]. Izd. in. lit., (1957).
2. Structurbericht, Zs. f. Kristallographie, 3, 168 (1935).
3. W. M. Meier, Z. Kristallogr., 113, 430 (1960).
4. A. G. Lundin and G. M. Mikhailov, Probory i tekhn. éksperimenta, 2, 90 (1960).
5. G. E. Pake, J. Chem. Phys., 16, 327 (1948).
6. A. G. Lundin, Dissertation. Krasnoyarsk, In. fiziki SO AN SSSR (1961).
7. K. S. Aleksandrov, A. G. Lundin, and G. M. Mikhailov, Kristallografiya, 5, 84 (1960) [Soviet Physics—Crystallography, Vol. 5, p. 77].
8. J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933).
9. G. V. Yukhnevich, A. V. Karyakin, N. I. Khitarov, and É. É. Senderov, Geokhimiya, 10, 849 (1961).
10. B. K. Vainshtein, Kristallografiya, 3, 293 (1958) [Soviet Physics—Crystallography, Vol. 3, p. 298].
11. P. Averbuch, P. Ducros, and X. Paré, Compt. rend., 250, 322 (1960).
12. S. P. Gabuda, A. G. Lundin, and G. M. Mikhailov (in press).
13. A. G. Lundin, G. M. Mikhailov, and S. P. Gabuda, Dokl. AN SSSR, 136, 869 (1961).
14. S. Yano, J. Phys. Soc. Japan. 14, 942 (1959).