

# Inelastic neutron scattering study of low frequency vibrations of water molecules in natrolite

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Incoherent inelastic neutron scattering results on the motion of water in the natural zeolite natrolite are presented. The measurements show two well resolved peaks at 68 and 87 meV, which indicates a single site location for the water molecule and excludes any clustering. The results are compared with i.r. and Raman studies and with frequencies observed in water and ice.

Представлены результаты воздействия некогерентного неэластичного нейтронного рассеяния на движение воды в природном цеолите натролите. Измерения показали наличие двух хорошо разрешенных пиков при 68 и 87 мэв, что свидетельствует о локализованном расположении молекулы воды и исключает образование кластеров. Результаты сравнены с результатами измерений методами ИК и Рамановой спектроскопии и с частотами, наблюдаемыми в воде и во льду.

Inelastic incoherent neutron scattering is a spectroscopic method [1, 2] which is very sensitive to the dynamics of hydrogen atoms, because the incoherent cross section of hydrogen is about ten times higher than that of other elements. Neutron spectra are not limited by selection rules or to certain optically active phases. Furthermore, the low frequency region is accessible by the application of low energy "cold" neutrons. Spectroscopic studies of water and ice indicated a clear separation between intra- (above 125 meV) and intermolecular vibrations (below 100 meV) [3]. The latter which consist of translations and hindered rotations of the H<sub>2</sub>O molecule are expected to be most sensitive to the nature and the symmetry of the environment of the water molecule and the nature of its bonds. Inelastic neutron scattering measurements [4] in water at different temperatures and on ice at -5°C showed only minor displacements of the peak corresponding to librational motion. The observed peak became however broader with increasing temperature.

A comparatively small shift was observed between water at 10°C (88 meV) and ice at -170°C (106 meV) [5], which suggests a certain similarity in the librational potential of the water molecule in different situations. The observed infrared and Raman spectra of H<sub>2</sub>O molecules in several zeolites are modified as compared to those of ice and water [6–8]. We therefore decided to study the motion of water in the natural zeolite natrolite (from Zálezly, Bohemia) by inelastic incoherent neutron scattering in the low frequency region. The measurements should provide information concerning the degree of rotational freedom of water molecules and the effect of types of binding upon the frequencies of librational motions, the distribution in time and space of the water molecules among the various possible lattice sites, the effect of their environment on the translational-vibrational mode of water molecules, and degree of association between the water molecules. The results have been compared to inelastic neutron scattering values on water and ice [4, 5, 9].

The crystal structure of natrolite Na<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>·2H<sub>2</sub>O, space group Fdd2, has recently been refined from neutron diffraction on a single crystal from the same location as our sample [10]. The chemical composition is stated there: 44.66% SiO<sub>2</sub>, 26.59% Al<sub>2</sub>O<sub>3</sub>, 14.26% Na<sub>2</sub>O, 0.02% TiO<sub>2</sub>, 2.60% CaO, 0.74% K<sub>2</sub>O, 0.14% P<sub>2</sub>O<sub>5</sub>, 0.01% Fe<sub>2</sub>O<sub>3</sub>, 0.01% MgO, 10.95% H<sub>2</sub>O. According to Breck [11] natrolite falls into the fifth structural group of zeolites with a characteristic fibrous habitus.

The group of aluminosilicate tetrahedra form small cavities in three-dimensional space in which the Na<sup>1+</sup> cations and the water molecules are located. Two water molecules and two Na<sup>1+</sup> ions are located in each cavity [12]. Complete ordering of Si and Al within the tetrahedra was observed [10, 12] in samples from the same locality as ours. The water molecule is hydrogen-bonded to the framework and the coordination sphere is completed by two sodium ions to form a tetrahedral arrangement around each oxygen of the water molecule [10–12].

## Experimental

Neutron time-of-flight measurements were performed at the rotating crystal spectrometer TOF2 installed at the cold source of the FR2 reactor of KfK, Karlsruhe. The sample container with the dimension (60 × 60 × 15) mm<sup>3</sup> was mounted in reflection geometry. The container was built from highly neutron absorbing cadmium metal in order to reduce background scattering from the container. The total volume available for the sample was subdivided by slices of cadmium into small areas of (60 × 1.5 × 1.5) mm<sup>3</sup> to reduce multiple scattering from the sample material. The front of the container was closed by an aluminium foil.

Data were recorded as energy gain spectra with an incident energy of 5.06 meV and 20 different angular positions between 80° and 166°. The time-of-flight spectra were converted

in the double differential scattering cross section from which we extracted the phonon density of states  $G(\hbar\omega)$  by iterative calculation and correction for multiphonon contributions.  $G(\hbar\omega)$  is the sum of the partial densities of the atomic components weighted with the scattering power and the vibrational amplitudes. The experimental energy resolution ranges from 3 to 10% for energy gain between 0 and 100 meV.

## Results

The resulting generalized phonon density of states is shown in Fig. 1a. Table 1 summarizes the observed lines from the neutron measurements which are compared to infrared and Raman data [7, 8] and to neutron data on water and ice [5].

The well resolved spectrum is characterized by five peaks in the frequency region from 0–100 meV. The two strong peaks at 68 and 87 meV are assigned to librations of the  $\text{H}_2\text{O}$  molecule about its  $a$  and  $c$  axes. The peaks at 13, 18, and 25 meV are explained by *Hughes et al.* [5] as translational vibrations of the  $\text{H}_2\text{O}$  molecules against an oxygen atom of the lattice. The spectra of ice at  $-5^\circ\text{C}$  and of water are represented in Fig. 1b for comparison. Maxima occur at 6.7 meV and about 32 meV in the translational part which goes up to 40 meV. In the librational range a splitting into 2 components is indicated with the main peak at 87 meV. For water between 2 and  $36^\circ\text{C}$  the peaks are broadened as compared with ice but occur

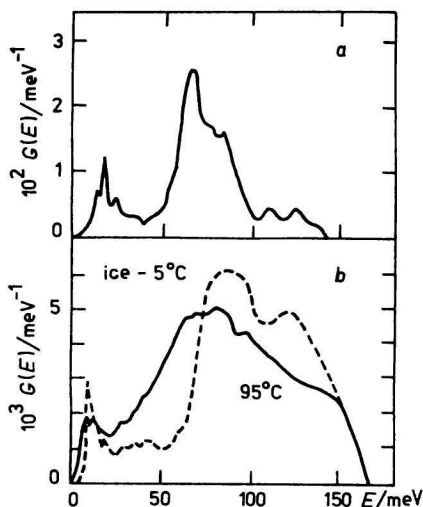


Fig. 1. Density of states in a) natrolite, b) water at  $95^\circ\text{C}$  and ice at  $-5^\circ\text{C}$ .  
 $G(E) = 1/\text{meV}$ .

Table 1

Comparison of the energies of observed neutron spectra and i.r. and Raman spectra

	Water	Water and ice	Natrolite	Natrolite	
	Neutron	Neutron	Neutron	IR	Raman
<i>T/K</i>	296	268	296		
	61	87	98	77.5	75
			68	60	60
	21	32	25	39	20.5
	8		18		18
	5	6.7	13		13.6
Ref.	[5]	[4]		[6]	[8]

at the same energies [4]. By comparison of the spectra of ice and natrolite two conclusions may be drawn:

1. The water molecules is located in a single site of the lattice.
2. No clustering of the H<sub>2</sub>O molecules is present.

### Discussion

The well resolved spectrum with two distinct lines at 68 and 87 meV indicates an ordered water molecule which occupies a single site in the structure. Another not equivalent molecule should give rise to an additional splitting. A higher degree of disorder with a distribution of H<sub>2</sub>O over several sites in the zeolite cavities shows a neutron spectrum which is very similar to that of water. Spectra of that nature have been observed at room temperature for the zeolites heulandite and stilbite [13], where only one broad maximum was observed at about 90 meV. This corresponds with the value of 87 meV observed in water [4] as indicated in Table 1. We conclude therefore that the H<sub>2</sub>O molecules in natrolite behaves differently from those in heulandite and stilbite and in water and ice. The ordering of H<sub>2</sub>O in natrolite is in agreement with the neutron structure determination [10].

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