STUDY OF THE HYDROCHLORIC ACID BY NEUTRON SCATTERING

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Phonon spectra of 2M, 3M, 4M, 6M and 8M aqueous solutions of HCl were measured by scattering of neutrons. The self-diffusion coefficient D_s between 2M and 6M increases with concentration and then at 8M abruptly falls to a value lower than at 2M. This can be explained by the appearance of a stable structure of the 8M hydrochloric acid which contains hexagonal rings composed of six molecules of water with a chlorine atom in the center of each hexagon.

1. Introduction

The investigation of atomic and molecular motion in water by thermal neutron scattering has been the subject of many papers (Refs. 1—5). However, none of these could precisely define the possible structure of water. With that purpose in mind we investigate water to which other atoms or molecules are added, and this allows indirect determination of the molecular structure of water. In the experiment reported here we used hydrochloric acid solutions. Such solutions are known to be dissociated, with both chlorine and hydrogen in the ionic state[6,7]. Different concentrations of the acid are used in the measurements performed by the scattering of slow neutrons. Our results are compared with an earlier result of Ref. 2.

2. Experimental

In obtainig the vibrational spectra of water solutions we used the time-of-flight spectrometer with a beryllium filter[8]. The mean energy of the incident slow neutrons is 5.1 meV, i. e., the incident wavevector is $k_0 = 0.159$ nm^{-1}. The resolution

of the apparatus was 0.3. Samples were contained in molybdenum containers 0.3 mm and 1.5 mm thick. The scattering angle Θ_{sc} is equal to 60°, i. e., the scattering vector is $Q = 0.159$ nm^{-1}. Thin, 0.3 mm thick samples were used in the measurements of the intensity of elastically scattered neutrons. The intention was to make the background as low as possible and thus the line width determination easier. Measurements of inelastic spectra were performed with 1.5 mm thick samples.

Measurements on hydrochloric acids of the following concentrations: 2M, 3M, 4M, 6M and 8M were carried out at room temperature. Spectra of a 3M solution were also measured, at the temperatures of 93 and 148 K. The inelastic spectrum was recorded in the interval between 7 and 150 meV. The spectrum of the incoming neutrons is precisely measured in the interval between 2.5 and 6 meV. The primary slow neutron spectrum was measured in straight transmission, and the line width was determined to be $\Delta E_p = 1.6$ meV.

All the scattered spectra were corrected for the background, chopper transmission function and detector efficiency.

Some attempts at multiple scattering calculation were undertaken using the Copley Monte Carlo programme[9]; for transmission geometry and a scattering angle of 60°, the corrections were of the order of 25% for larger energy transfer. If was found that such corrections did not change the position of the peaks in the inelastic spectra, which is the important factor in our analysis.

3. Results and analysis of the elastically scattered spectrum

The spectra of the elastically scattered neutrons presented in Figs. 1a and 2b show the whole primary spectrum. Other figures present only parts at the half-maximum of the spectrum. The broadening ΔE of each line in relation to the primary spectrum is given in Table 1. In the analysis of the elastically scattered spectrum, two models were used of continuous diffusion of molecules and the quasi-crystalline structure model[10]. In the case of the first model, the line width is given by

$$\Delta E = 2\hbar\, D_s Q^2 \tag{1}$$

and in the second model as:

$$\Delta E = \frac{2\hbar}{\tau_0}\left[1 - \frac{e^{-2W}}{1 + Q^2 D_s \tau_0}\right] \tag{2}$$

where D_s is the self-diffusion coefficient and $2W$ is the Debye-Waller factor.

According to the first model the molecules are in continuous diffusion. According to the second model, the molecules vibrate around an instantaneous equilibrium position for a time τ_0 and then make a large diffusion jump for a time τ_1. The model assumes that $\tau_1 \ll \tau_0$. This assumption that the short-time (τ_1) and intermediate time (τ_0) diffusion of water molecules are distinguishable at lower temperatures is more justified then at room temperature[11]. The calculations of the self-difussion constant D_s for water were made on the basis of the second model and the values of D_s are found to be in agreement with the result of earlier work[2].

A small difference in the result is most probably a consequence of the relatively poor resolution of the time of flight spectrometer we used. We applied the calculation to all concentrations. The values for D_s obtained on this basis are presented in Table 1.

TABLE 1.

Quantities	pure water	HCl concentration				
		2M	3M	4M	6M	8M
ΔE (eV)	0.44	0.18	0.27	0.18	0.24	0.10
$D_s \cdot 10^{-5} \left(\dfrac{cm^2}{s}\right)$	1.40	0.58	0.89	0.58	0.75	0.31
$\tau_0 \cdot 10^{-12}$ (s)	0.80	1.91	1.24	1.90	1.47	3.54

Line broadening ΔE, self-diffusion constant D_s, and relaxation time τ_0 for different concentrations M of HCl — water solutions.

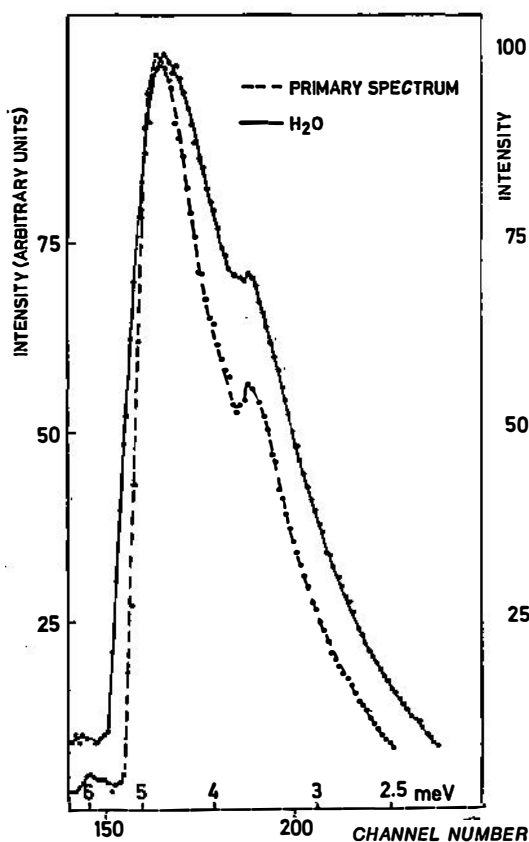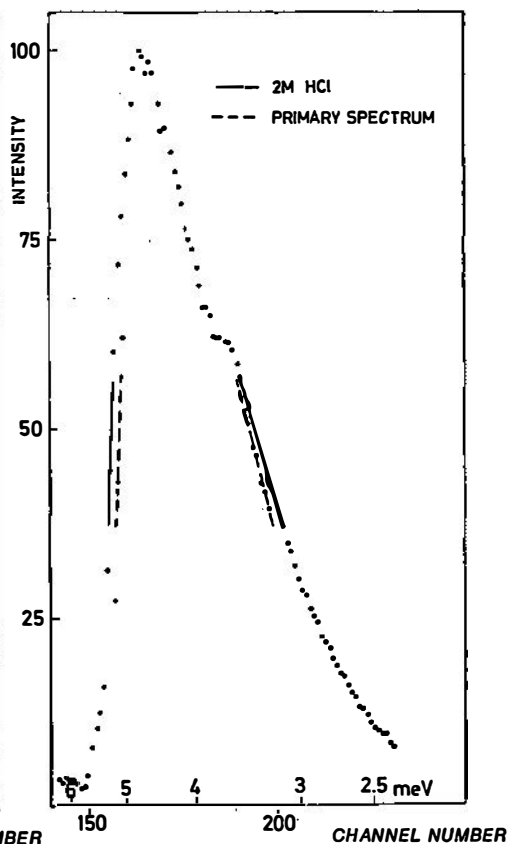Fig. 1a. Experimentaly determined primary spectrum with spectrum of H_2O.

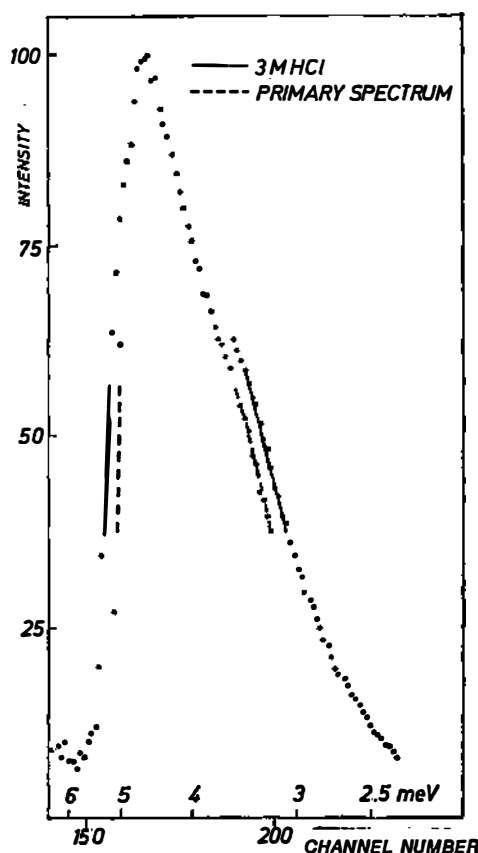Fig. 1b. Experimentaly determined primary spectrum with spectrum of 2M HCl.

Fig. 1c. Experimentaly determined primary spectrum with spectrum of 3M HCl.

An average length of the diffusion jump for water was found to be 0.08 nm, which is somewhat smaller than the value in Ref. 2. The reason for this difference is most probably in our inability to determine the τ_1 value.

The hydrogen chloride molecules added to water will lower the self-diffusion constant and increase the time for which the water molecules vibrate around the instantaneous equilibrium position. This is expected since the chlorine atom is heavy. Especially interesting is the five times decrease of D_s at 8M HCl as compared to the pure water. The decrease of D_s in the 6M solution is only double. A similar situation takes place with time τ_0. Obviously an abrupt decrease in the ability of molecules to diffuse occurs for solution between 6M and 8M, and an increase of a time τ_0. By analyzing these systems, we conclude that close to 7M there are 6 molecules of water in relation to every chlorine atom. This suggests the possibility of the existence of hexagonal rings composed of 6 molecules of water, which diffuse along with the hydrogen ions. This does not exclude the possibility of decomposition of these rings, or breaking off of its parts at some rate, i. e., depending on the temperature. Namely, water molecules[7] are entering and leaving the neighbourhood of a chloride ion an a time scale of $\sim 10^{-12}$ s.
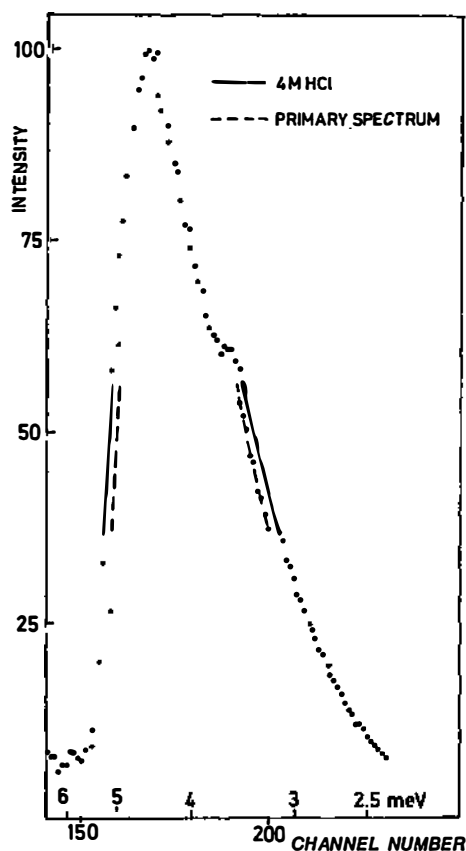
Fig. 2a. Comparison of experimental data for 4M HCl compared with primary spectrum.
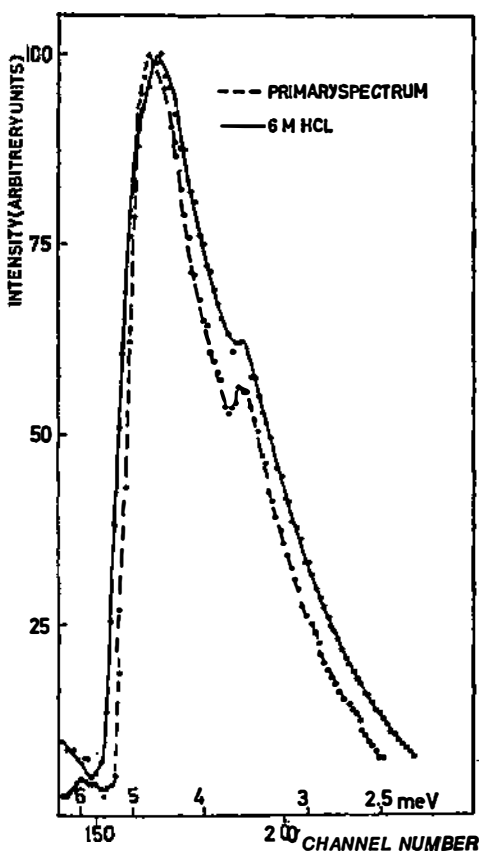
Fig. 2b. Comparison of experimental data for 6M HCl compared with primary spectrum.

By analyzing the dimensions of the hydrogen and oxygen atoms and the chloride ion we concluded that the central part of the hexagonal ring could very easily accept the chloride ion, which then considerably slows the diffusion and the disintegration of the molecular structure. This can be seen in the elastic as well as in the inelastic part of the spectrum. An illustration of such structure is given in Fig. 3. Six other hydrogen atoms, which were not shown in Fig. 3, lie in the horizontal plane of the hexagonal ring, i. e. three above and three below plane and angle of 104.5' between HOH molecule.

Larsson[2] used a gas model for the calculation of the average energy of the scattered neutrons and compared the results with the experimental data. With mass of water molecules of 18 atomic units he found a significant disagreement between the experimental data and the theory. Fitting with mass m equal to 100 gave a much better agreement.

Our calculation used for the mass of water $m = 108$ $(= 6 \times 18)$ and we obtained an excellent agreement. This is the mass of the hexagonal ring, mentioned above, which confirms the existence of such structure in water.
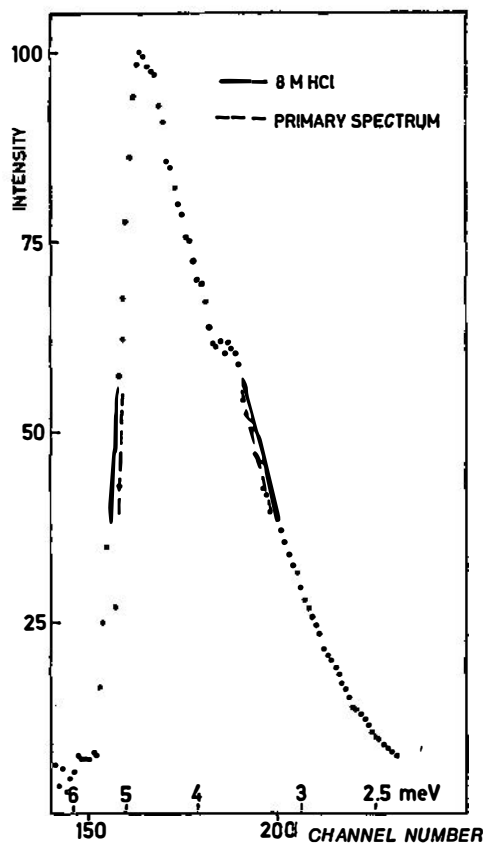
Fig. 2c. Comparison of experimental data for 8M HCl compared with primary spectrum.

4. Analysis of the inelastically scattered spectrum

The intensity of the incoherently scattered neutrons i. e. the frequency spectrum $f(\omega)$ is given mainly by the scattering law for the one phonon processes:

$$I_{incoh} \sim S(Q, \omega)_s \, af(\omega) \qquad (3)$$

and therefore the intensity I_{incoh} of the incoherently scattered neutrons measures the phonon energy distribution [lattice vibration spectrum $-f(\omega)$]. Fig. 4 shows the spectrum of the inelastically scattered neutrons from 2M 4M, 6M, 8M solutions and Fig. 4 the spectra of the 3M solution at temperatures 93 and 148 K. Fig. 5 does not include the spectrum of the 3M solution. According to the intensity its place is in between 2M and 4M spectra.

We see in Fig. 5 that the intensity of the spectra increases from 2M towards 6M and that at 8M it falls below the intensity of the 2M solution. The abrupt fall of the phonon population could indicate the formation of a stable structure such as shown in Fig. 3.
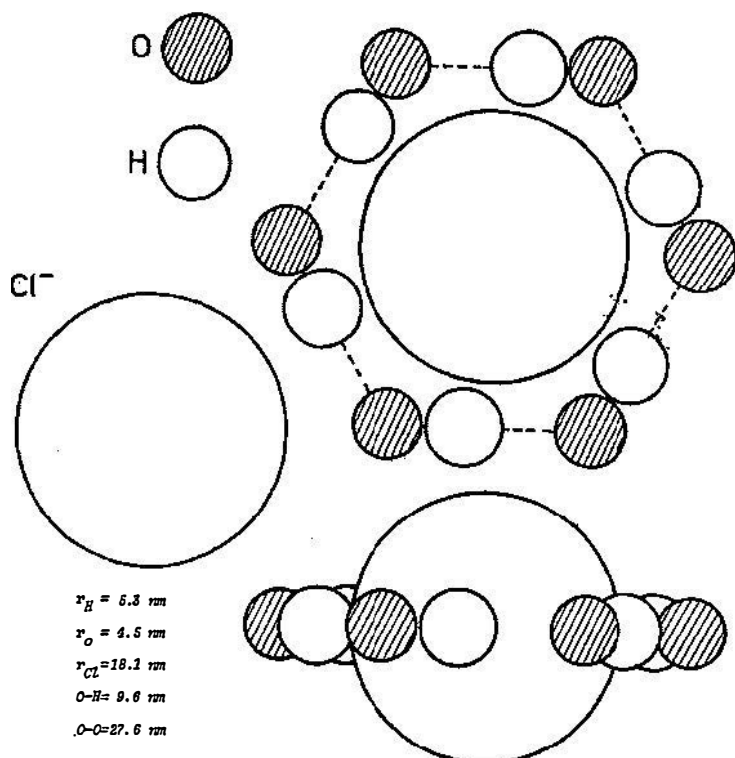

Fig. 3. Two dimensional schemes of liquid structure HCl in water with corresponding parameters.

Some of the terms found in the spectra lying at: 8.4 9.2 22 28 34 and 63 meV can be found in the spectrum of pure water. Terms which do not exist in water lie at 11.5, 15 and 42 meV; the last of which is especially pronounced — very sharp — with an abrupt fall of intensity. This vibration surely reflects the motion of the chlorine atoms. It also appears in the 3M solutions at the lower temperatures. An abrupt fall of intensity of this peak cannot be found in the 8M HCl spectra at 93 K, although the peak persists. This, also, is a proof of the formation of a stable structure.

The peak, formerly identified in the case of water as the rotation term, in our spectra mildly splits off in the upper part at 63 and 53 meV. In the spectra at low temperatures there is only one peak at 63 meV, indicating that it is made of two attached peaks representing a hindered rotation, while the peak at 53 meV reflects free roations.
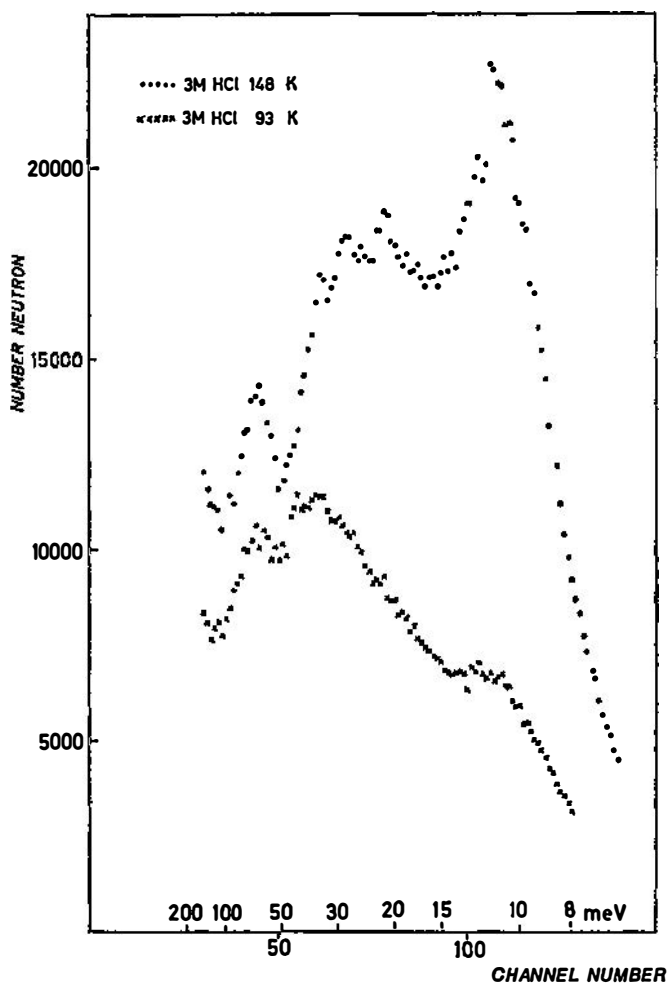
Fig. 4. Comparison of experimental data for two different temperatures for 3M HCl.

5. Conclusions

In conclusion we would like to stress that the spectra of the HCl solutions when compared with the spectrum of pure water show some interesting features.

Notably, the line width, the self-diffusion coefficient D_s and the time for which the molecules vibrate around an instantaneous equilibrium position show an increase from 2M to 6M solution and an abrupt fall at the 8M HCl. The intensities of inelastically scattered neutrons behave similarly. All this points unambi-
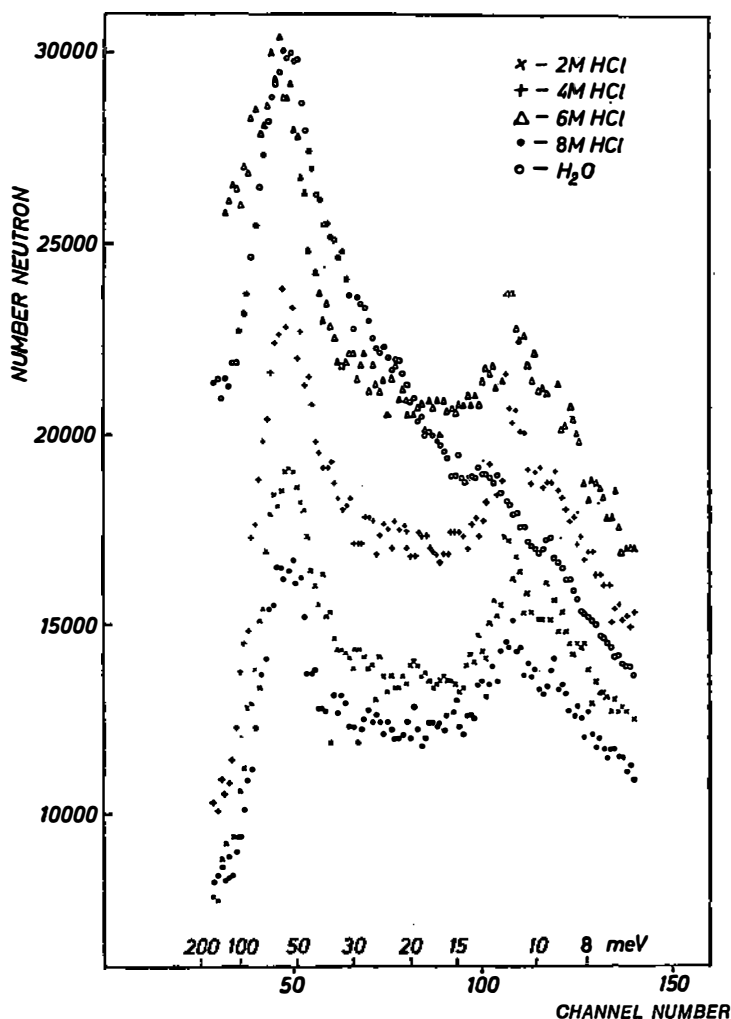
Fig. 5. The I_{incoh} at four concentrations of HCl, measured with the incident wavevector $k_0 = 0.159 \, nm^{-1}$, compared with primary spectrum.

guously to the formation of a stable structure with 6 molecules of water and one chloride ion, as shown in Fig. 3. One of the proofs for the existence of the hexagonal rings is the gas model calculation, with the water mass of 10%, which gives good agreement with the experiment. After melting, the structure of ice is decomposed into the hexagonal rings which diffuse among themselves. The spectra show a distinct vibration, which represents motion of the chlorine atom, at an energy of 11.5 meV. The rotational term at 63 meV found by Raman spectroscopy, points to the existence of two peaks originating from hindered and free rotation.

All the peaks in the spectra of frozen hydrochloric acid can be found in the spectra of liquid hydrochloric acid as well.

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PROUČAVANJE HLOROVODIČNE KISELINE METODOM NEUTRONSKOG RASEJANJA

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Mereni su fononski spektri 2M, 3M, 4M, 6M, 8M hlorovodične kiseline. Primećeno je da koeficijent samodifuzije, D_s, između 2M i 6M HCl raste sa koncentracijom, a onda naglo pada na 8M HCl. Ovo se može objasniti građenjem stabilne strukture na 8M HCl koja se sastoji od heksagonalnog prstena vode, a u centru tog prstena je hlorov jon.