

## DYNAMICAL ASPECTS OF PHASE TRANSITIONS IN PERCHLORIC ACID MONOHYDRATE

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Neutron inelastic incoherent scattering was measured for solid perchloric acid monohydrate at various temperatures and also for the liquid perchloric acid monohydrate. For phase II, the  $H_3O$ -torsional peak corresponding to uniaxial torsion around the triple axis, appears at  $560\text{ cm}^{-1}$ , and it is quite narrow. For phase I this peak smears out and shifts to *ca*  $520\text{ cm}^{-1}$  in agreement with interpretation that rotational motions are many axial for this phase. For liquid substance, this peak shifts towards higher energies ( $600\text{ cm}^{-1}$ ) and the spectrum resembles that of water. Broadening of Be-edge is visible for phase I, indicating rotational jumps. Integrated intensities of elastically scattered Be-spectrum are for phase I significantly smaller than those for phase II indicating a lowering of Debye temperature when passing from phase II to I. A comparison with NMR and IR published data was made. Barriers to  $H_3O$ -rotation are estimated for phases II and I; they are: 4.6 and 3.9 kcal/mole.

### 1. Introduction

Besides the melting point at  $+50^\circ\text{C}$  the condensed perchloric acid monohydrate has another phase transition point at about  $-25^\circ\text{C}$ . The first information about this point was given by Taylor and Vidale [1] and Rosolovskii and Zinovev [2].

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An X-ray diffraction study performed by Lee and Carpenter [3] for phase I and separately by Nordmann [4] for phase II led to the conclusion that the structures in the two phases are different. Namely phase I is orthorhombic (space group Pnma) with the following parameters of the unit cell:  $c = 7.339 \text{ \AA}$ ,  $a = 9.065 \text{ \AA}$ ,  $b = 5.569 \text{ \AA}$ . Phase II, on the other hand, is monoclinic (space group P2<sub>1</sub>/n) with the following unit cell parameters:  $a = 7.541 \text{ \AA}$ ,  $b = 9.373 \text{ \AA}$ ,  $c = 5.359 \text{ \AA}$ ,  $\beta = 97^\circ 41'$ .

In the two structures one may easily find layers of ClO<sub>4</sub><sup>-</sup> ions and H<sub>3</sub>O<sup>+</sup> ions. In the orthorhombic phase an orientational disorder was suggested for protons of the H<sub>3</sub>O groups. For monoclinic phase, on the other hand, hydrogen atoms have well-defined positions lying nearly on lines connecting oxygen of the H<sub>3</sub>O<sup>+</sup> group with oxygens of three neighbouring ClO<sub>4</sub><sup>-</sup> groups.

The crystallographic situation described above allows us to expect that there should be changes in the dynamical behaviour of H<sub>3</sub>O groups at the phase transition. This was indeed proved by NMR measurements made by Hennel and Pollak-Stachura [5] and by O'Reilly *et al.* [6]. Under study were both the NMR line shape and the relaxation time  $T_1$ . Line shapes differed for the two phases: for phase II it is consistent with the picture that the H<sub>3</sub>O group reorients around an axis perpendicular to the proton plane; in phase I the line shape is consistent with the picture that the H<sub>3</sub>O group isotropically reorients, *i. e.* the reorientation is no longer uniaxial.

From NMR measurements it was also possible to estimate the barriers of reorientation: the values for phase II were 3 kcal/mole [5] and 4.8 kcal/mole [6]; the barrier value for phase I as given in [6] is 4.2 kcal/mole. It should be noted that total neutron scattering cross-section experiments performed by J. M. Janik *et al.* [7] led to the barrier value for phase I of 1.8 kcal/mole, which should be treated as an estimate only because of a calibration procedure not very well suited to H<sub>3</sub>O<sup>+</sup> ions.

If there is a difference as described above in the reorientational possibilities of H<sub>3</sub>O groups in the two phases one should expect that it would lead to differences in the phonon spectrum as measured by neutron inelastic incoherent scattering. In particular, the torsional vibrations of H<sub>3</sub>O groups should be different in the two phases. This stimulated the neutron scattering experiments presented in the present paper. Besides measurements below and above the phase transition point at about  $-25^\circ\text{C}$ , also a measurement for the liquid perchloric acid monohydrate was performed.

## 2. Experimental

Neutron inelastic incoherent scattering measurements were made by using a time of flight spectrometer with the Be-filter in inverted geometry installed at the pulsed reactor of the Joint Institute of Nuclear Research at Dubna. The perchloric acid monohydrate was placed in a flat aluminium sample-holder in such a manner that both the sample holder and the sample were heated above the melting point of the substance and the liquid sample was poured onto the sample holder. Afterwards the substance froze when the temperature was reduced. The whole procedure was performed in a dry box in the atmosphere of dry nitrogen. The tightly closed sample holder was then put into a thermo-

stat in which it was possible to obtain any temperature in the region from liquid nitrogen to *ca.* +100°C. Both the neutron spectrometer and the thermostat have been described in detail elsewhere [8], [9].

Measurements were performed for five temperatures: -150°C and -50°C for phase II, -15°C and +21°C for phase I, and +60°C for the melted substance.

### 3. Results and discussion

Results in the form of scattered neutron intensity *vs* channel number (indicating the time of flight of neutrons incident to the sample) are presented in Fig. 1.

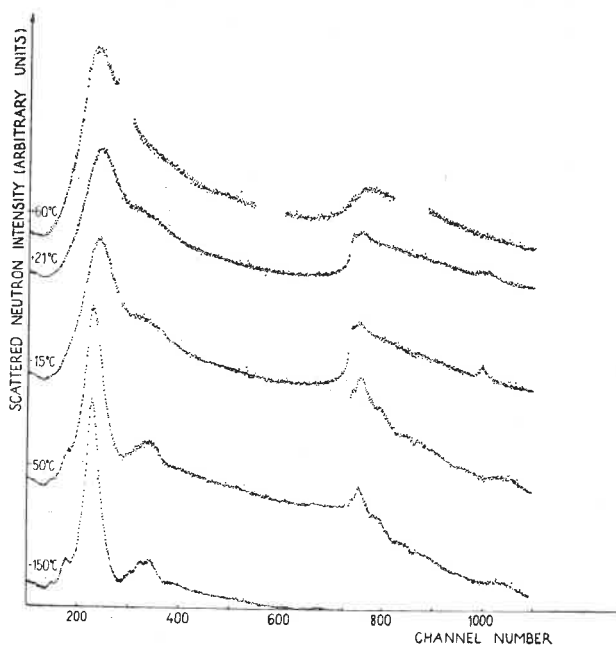


Fig. 1. Intensity of neutrons scattered by perchloric acid monohydrate at various temperatures *vs* channel number. Background subtracted

Fig. 2 presents the same results transformed into the phonon density function on the basis of a one phonon transformation formula [10].

The following experimental facts may be observed from the results obtained:

1) The inelastic spectrum which shows a distinct peak structure at the lowest temperature is more and more smeared out as the temperature increases.

2) The most intense peak in the inelastic spectrum which is unquestionably connected with torsional motion of the  $\text{H}_2\text{O}$  group (in the solid substance) shows an unchanged position ( $560\text{ cm}^{-1}$ ) for the two spectra corresponding to phase II ( $-150^\circ\text{C}$  and  $-50^\circ\text{C}$ ). For the phase I ( $-150^\circ\text{C}$  and  $+21^\circ\text{C}$ ) this peak shifts towards lower energies ( $520\text{ cm}^{-1}$ ) and is significantly broadened. For the melted substance the peak remains broad but shifts back to higher energies (*ca.*  $600\text{ cm}^{-1}$ ).

3) The beryllium edge, which is very sharp in phase II, shows a distinct tail in phase I, thus indicating the Lorentzian type of broadening. This broadening becomes much more significant for the melted substance.

4) On the Maxwellian tail of the beryllium cut-off one may see peaks arising from Bragg-reflections from the substance. It is evident that these Bragg-reflections appear in

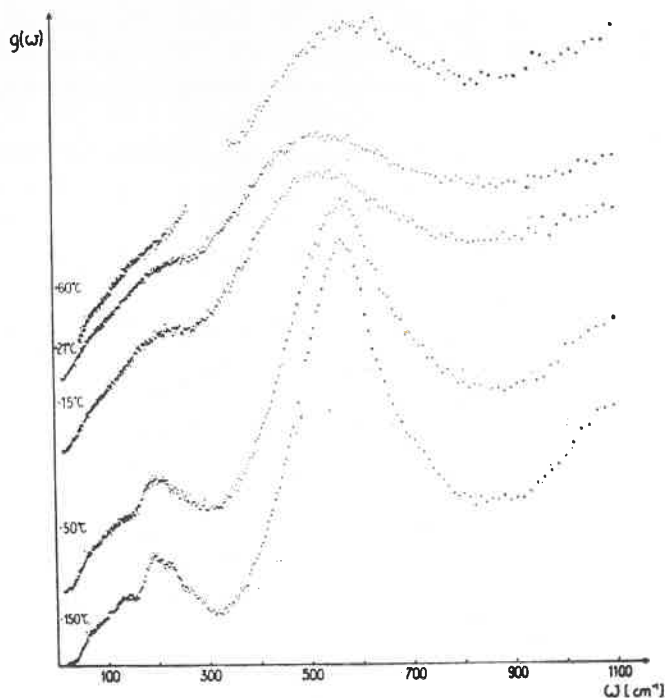


Fig. 2. Phonon density function obtained for perchloric acid monohydrate at various temperatures from results presented in Fig. 1

different positions in phase II from those in phase I, indicating the difference of structure of the two phases.

An explanation of the behaviour described in point 2 may be deduced from the results of NMR [5], [6] as pointed out in Section 1. The sharp torsional peak at  $560\text{ cm}^{-1}$  in phase II corroborates the assumption of a well-defined, uniaxial torsional oscillation of the  $\text{H}_3\text{O}$  group. In phase I the situation of the  $\text{H}_3\text{O}$  group becomes much less defined. The group performs many axial torsional motions leading to a broadening of the peak and also, due to weaker acting forces, the average frequency is reduced to  $520\text{ cm}^{-1}$ .

An estimation of the barrier to rotation is possible, if one assumes the high barrier approximation which allows the use of the formula

$$\nu_{\text{tors}} = 2n \sqrt{V_0 \cdot B}$$

where  $\nu_{\text{tors}}$  is the torsional frequency,  $n$  is the symmetry number,  $V_0$  is the barrier height, and  $B$  is the rotational constant.

Taking  $n = 3$  and a rotational constant corresponding to the moment of inertia of the  $\text{H}_3\text{O}$  group around the triple symmetry axis, we have for phase II ( $\nu_{\text{tors}} = 560 \text{ cm}^{-1}$ )  $V_0 = 4.6 \text{ kcal/mole}$ , and for phase I ( $\nu_{\text{tors}} = 520 \text{ cm}^{-1}$  but the  $n = 3$  assumption is now questionable!)  $V_0 = 3.9 \text{ kcal/mole}$ . These values are in relatively good agreement with previously quoted NMR [6] values (4.8 and 4.2 kcal/mole).

This situation is in accordance with the behaviour of the beryllium cut-off as described in point 3. The sharpness of the Be-edge in phase II indicates that there are very rare rotational jumps for the  $\text{H}_3\text{O}$  group in this phase. In phase I, on the other hand (in agreement with the lowering of the rotational barrier), the  $\text{H}_3\text{O}$  group begin to reorientate by jumps which causes a Lorentzian broadening of the Be-edge.

When the substance is melted we have the situation already well-established by physico-chemical measurements [11] in which the  $\text{H}_3\text{O}$  groups no longer exist but the substance is rather a solution of  $\text{HClO}_4$  molecules in water; therefore it is then natural to expect that there will be a great resemblance of the neutron spectrum to that of water. Indeed the positions of torsional peaks for our melted substance practically coincide with the position of the hindered rotation peak as measured for water by many authors [12]. It is also natural that the beryllium edge for the melted substance is very broad; this is due the diffusive motions which are switched on after melting.

Generally speaking, the neutron spectrum measured for room temperature agrees well with previously reported neutron spectra for the same substance [13], [14].

It is interesting to compare the positions of peaks which may be seen in our phonon density spectrum for the lowest temperature with those reported by Savoie and Giguere [15] in their infra-red data. Our first peak (or rather distinct shoulder) at about  $60 \text{ cm}^{-1}$  could not be detected by their infra-red equipment. Our next peak appears at *ca*  $140 \text{ cm}^{-1}$  and perhaps could be compared with their  $125 \text{ cm}^{-1}$ . Our third peak corresponds to *ca*  $200 \text{ cm}^{-1}$ , which perhaps may be connected with the infra-red doublet at  $192/205 \text{ cm}^{-1}$ . There is very uncertain evidence of further peaks in this region in our neutron spectrum. Infra-red data, on the other hand, give here peaks which were interpreted as  $\text{H}_3\text{O}$  translatory modes. It should be pointed out that a large dispersion of translatory phonon modes must be expected thus leading to great deviations from coincidence of neutron and infra-red spectra in this region.

Our main peak at  $560 \text{ cm}^{-1}$  appears only as a weak one in infra-red, which confirms our interpretation that it is connected with  $\text{H}_3\text{O}$  torsional motion around the triple symmetry axis, as such a peak should be forbidden in infra-red.

The shoulder which we observed at about  $700 \text{ cm}^{-1}$  corresponds, on the other hand, to the infra-red peak at  $680 \text{ cm}^{-1}$  which was interpreted as  $\text{H}_3\text{O}$  torsion around other axes.

#### 4. Conclusions

The main results of the present paper may be summarized as follows:

1) Neutron inelastic incoherent spectra confirm the results previously reported from NMR measurements. They agree with the assumption that the  $\text{H}_3\text{O}$  group in perchloric acid monohydrate performs uniaxial torsional oscillation with rare rotational jumps at

phase II, whereas in phase I the H<sub>3</sub>O situation is orientationally disordered and much more frequent reorientational jumps occur. The barrier values for reorientation in both phases agree well with those reported from NMR.

2) A comparison of the present neutron spectra and the infrared spectra leads to the conclusion that H<sub>3</sub>O torsional modes have a significant dispersion. The rotatory modes on the other hand, are rather flat. A comparison between the intensity of the 560 cm<sup>-1</sup> rotatory mode in neutron scattering and that in infra-red confirms the interpretation that it is connected with torsion around the triple symmetry axis of the H<sub>3</sub>O group.

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