REORIENTATION OF THE H_3O^+ ION IN POLYCRYSTALLINE PERCHLORIC ACID MONOHYDRATE STUDIED BY NMR

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The proton magnetic resonance absorption line in polycrystalline $HClO_4.H_2O$ was measured between $-180°C$ and $+50°C$. Two distinct line width transitions were found. In the lowest temperature the line corresponds to an equilateral triangle of side $r = 1.7$ Å formed by the protons in the OH_3^+ group. Second moment considerations led to the conclusions that in the intermediate region (between $-90°$ and $-40°C$) the triangle rotates about perpendicular axis and above $+5°C$ it reorients isotropically. A thermal hysteresis of the line width found between $-30°C$ and $0°C$ corroborates the conclusions of Rosołowskij and Zinovjev concerning a first order phase transition in this region.

Introduction

X-ray studies of the $HClO_4 \cdot H_2O$ crystal (Volmer 1924, Lee and Carpenter 1953) lead to the hypothesis that its lattice is composed of two ionic groups, ClO_4^- and H_3O^+. Because the X-ray method is somewhat inefficient in giving reliable information about the positions of the protons, the existence of the H_3O^+ groups in this crystal had to be confirmed by other methods.

Kakiuchi *et al.* (1952), Kakiuchi and Komatsu (1952) and Richards and Smith (1951) studied the shape of the proton magnetic resonance line of $HClO_4 \cdot H_2O$ at liquid nitrogen temperature. Comparing the line shape with the theoretical results of Andrew and Bersohn (1950) and calculating the second moment of the line, the authors were able to confirm without doubt the existence of H_3O^+ groups in which the protons form an equilateral triangle with a side $r = 1.70$ Å. The authors also observed a much narrower, structureless line at room temperature.

Till now no extensive studies of the width and shape of the proton NMR line in $HClO_4 \cdot H_2O$ as a function of temperature have been performed, while the crystal structure has been studied by other methods. Infra-red absorption and Raman studies led to conclusions concerning the disorder of H_3O^+ group orientations at room temperature (Mullhaupt

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and Horning 1956, Taylor and Vidal 1956). These studies also gave some uncertain evidence of phase transitions between — 50 and —20°C. Rosołowskij and Zinovjev (1958) found a first order phase transition at —24.4°C, using the calorymetric method. They also found a slight change of density at that temperature. Investigations of inelastic scattering of cold neutrons by Janik (1964) and Janik *et al.* (1965) led to conclusions concerning torsional vibrations of the H_3O^+ group and made possible the determination of the height of the barrier to rotation as 1.8 kcal/mol.

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Experiments and results

In this work the proton magnetic resonance absorption line derivative was measured between —180°C and the melting point of $HClO_4 \cdot H_2O$, which is +49.2°C. Examples of the obtained derivative curves are shown in Fig. 1. Fig. 2 presents the second moment values

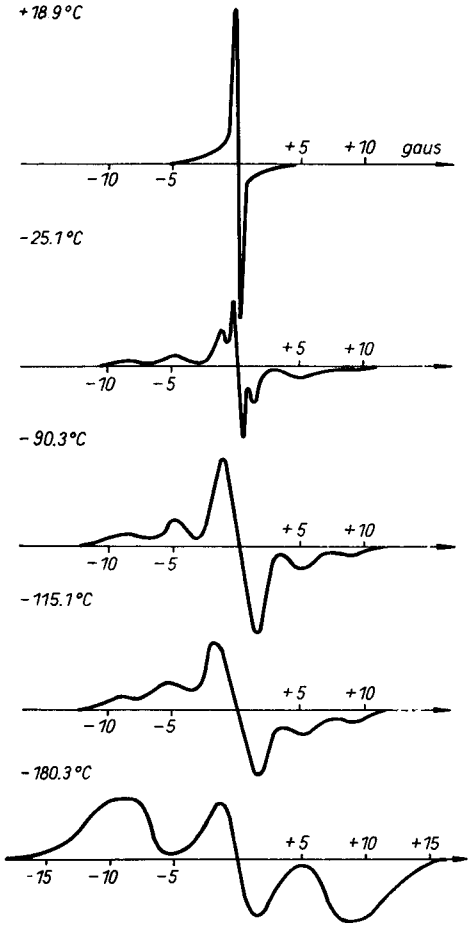

Fig. 1. Proton magnetic resonance in polycrystalline $HClO_4.H_2O$. Derivatives of the absorption line at different temperatures

corrected for the influence of modulation by means of the Andrew's formula (1953). The main feature of Fig. 2 its that there are two distinct line width transitions.

A conventional NMR broad line spectrometer employing the Pound-Watkins marginal oscillator was used. The applied magnetic field was 4097 gauss, while its inhomogeneity did not exceed 0.1 gauss over the sample volume (about 3 cm^3). The field was swept over 40 gauss within 25 min. The modulation frequency was 71 c/sec and its amplitude varied between 0.18 and 1.4 gauss.

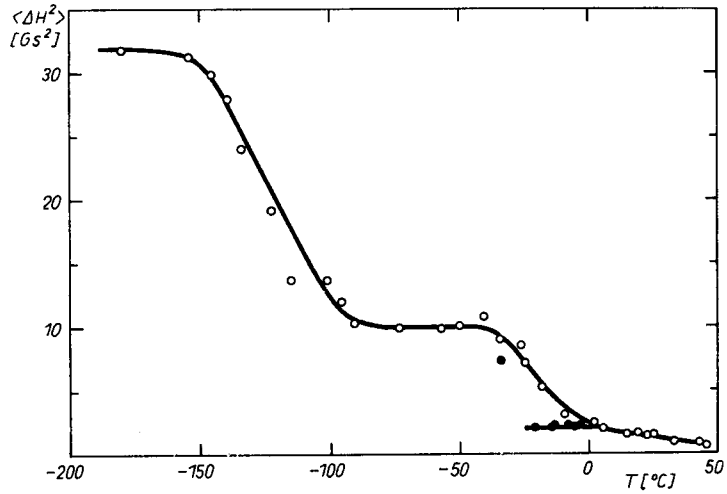

Fig. 2. Second moment of the absorption line in polycrystalline $HClO_4.H_2O$ measured at different temperatures

Some of the lines were measured at two different values of the high frequency amplitude H_1 but no changes in their shape and width were observed. This means that there was no great saturation. The time constant of the "lock-in" phase sensitive detector was 1 sec. The temperature control of the head containing the sample was performed in a manner described elsewhere (Hennel *et al.* 1965). The temperature inside the head was measured by means of a copper-constantan thermocouple.

Discussion

a. The broad line region (below −150°C)

In this region the obtained line shape corresponds closely to that predicted for an equilateral triangle of side r formed by three like spins 1/2 (Andrew and Bersohn 1950). The best fit to the experimental line shape is obtained with $r = 1.70$ Å and $\beta^2 = 2.3$ gauss^2, β^2 being the second moment due to interaction with neighbouring groups. This value of r is exactly the same as that found by Kakiuchi *et al.* (1952).

Also the second moment consideration corroborates the hypothesis of the existence of H_3O^+ groups. Assuming the value $r = 1.70$ Å and the crystallographical data given by Volmer (1924) and Lee and Carpenter (1953), one gets 29.6 gauss^2 for the second moment

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due to interaction within the triangle, 2.3 gauss^2 due to interaction with protons in neighbouring groups, and 0.01 gauss^2 due to interaction with the chlorine nuclei. Summing these values, one gets 31.91 gauss^2 giving agreement with the experimental value 31.8 gauss^2.

b. Intermediate region *P* (between −90 and −40°C)

In this region the second moment corresponds to a rotation of the H_3O^+ group about an axis fixed in space and perpendicular to the plane of the equilateral triangle formed by the three protons. According to simple calculation, the assumed rotation of the triangle should reduce the intraionic part of the second moment four times, *i. e.* to the value 29.6/4 = 7.4 gauss^2. Assuming the second moment due to interaction with neighbouring nuclei to be 2.2 gauss^2 (see next paragraph), the value 9.6 gauss^2 is obtained, giving good agreement with the experimental one, 10.0 gauss^2.

c. Narrow line region, above +5°C

As the results of the second line width transition, the second moment is reduced to the value 2.2 gauss^2, which can be accounted for by the interactions with nuclei neighbouring the H_3O^+ group. Further decrease in this value to be seen in Fig. 2 may be caused by diffusion of H_3O^+ ions through the lattice.

The evident lack of any contribution to the second moment caused by the intraionic interactions means that the H_3O^+ group undergoes isotropic reorientation. It is likely that the triangle now rotates about an axis which reorients its direction with a correlation time shorter than the reciprocal intermediate line-width, *i. e.* 3×10^{-5} sec.

d. First line width transition (between −150 and −90°C)

In this region the reorientation of the triangle discussed in section "*b*" becomes fast enough to have an influence on the line-width. The reorientation frequency ν_c calculated according to the theory of Gutowsky and Pake (1960) ranges between 1.37×10^5 c/sec and 4.27×10 c/sec and follows the Arrenius law $\nu_c = \nu_0 \exp(-E/RT)$ with the value of the activation energy $E = 3$ kcal/mol. This value must be considered as a rough estimation because the line shape was not gaussian.

e. Second line width transition (between −40 and +5°C)

In this region the open circles shown in Fig. 2 were obtained during heating and the black ones during cooling of the sample. The evident thermal hysteresis corroborates the conclusion of Rosołowskij and Zinovjev (1958) about first-order phase transition in this region.

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