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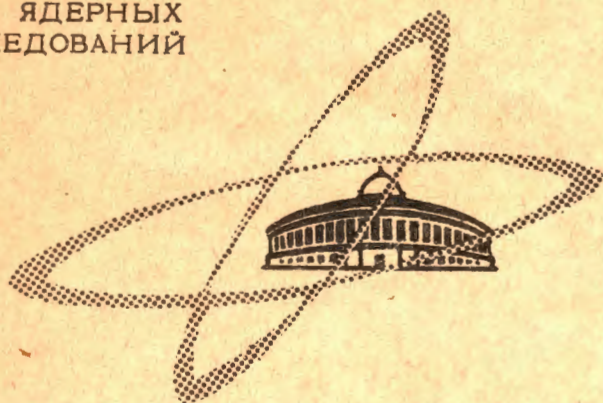
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ЛАБОРАТОРИЯ НЕЙТРОННОЙ ОПТИКИ

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DETERMINATION OF PARAMETERS OF THE
ROTATIONAL DYNAMICS OF GROUPS NH_4 IN
 NH_4ClO_4 AND H_2O IN H_2OClO_4 BY MEANS OF
INELASTIC SCATTERING OF NEUTRONS

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ОБЛАСНОЕ ЦЕНТРАЛЬНОЕ УЧЕБНО-НАУЧНОЕ
ИССЛЕДОВАТЕLSКОЕ ЦЕНТРАЛЬНОЕ
БИБЛИОТЕКА

1. Introduction

The existence of an H_2O group in perchloric acid monohydrate may be considered as an experimentally well-established fact^{/1-4/}. It has also been proved that H_2OClO_4 and NH_4ClO_4 , which belong to the orthorhombic crystallographic system, possess practically identical lattices of ClO_4^- ions^{/1,3/}. This means that the H_2O and NH_4 groups in the two substances are situated in almost the same surrounding conditions.

It is interesting to compare the dynamic properties of the NH_4 and H_2O groups in these crystals, paying special attention to the rotational possibilities of the groups. The information which has been obtained in connection with this problem comes from three types of investigation i.e. those made by applying the Raman technique^{/5/}, the NMR technique^{/6-9/}, and the neutron scattering technique^{/10-13/}.

The following results have been obtained for NH_4ClO_4 : a relatively narrow proton resonance line leads to low values of the so-called second moment $(\Delta H)^2$. These values are: $2,42 \text{ Oe}^2$ for the temperature 20°K (Richards and Schaefer^{/7/}), and $1,27 \text{ Oe}^2$ and $1,18 \text{ Oe}^2$ for temperatures 70°K and 298°K (Ibers^{/6/}). The barrier to rotation evaluated for NH_4ClO_4 from these results is, according to Ibers, 2 kcal/mol ; according to Richards and Schaefer on the other hand it is less than 1 kcal/mol . Ibers' evaluation leads to the conclusion that the rotation of the NH_4 group is hindered, Richards and Schaefer's value suggests freedom of rotation, Neutron investigations give further arguments strongly supporting a low value of the barrier to rotation; these arguments are: a high value ($13 \text{ b}/\text{\AA}^2$) of the slope of linear dependence between the total neutron scattering cross-section and the neutron wavelength in the subthermal neutron energy region (Rush et al.^{/11/}) leads to the conclusion that the rotation of NH_4 groups in NH_4ClO_4 is free, and to an evaluation of the barrier value for $0,1 - 0,2 \text{ kcal/mol}$. Also the neutron spectrum obtained by the scattering of cold neutrons from a crystalline NH_4ClO_4 (Janik et al.^{/12/}) shows no sharp peaks from which the existence of discrete torsional oscillation levels could be deduced. Thus, if the high barrier value suggested by Ibers is not taken into account, all other experiments lead to the conclusion that the rotation of NH_4 groups in NH_4ClO_4 is free.

Much less clear is the situation in H_3OClO_4 ; although from experiments performed by applying the Raman technique^{/2/, /14-16/, /5/} many frequencies may be identified as those caused by the H_3O^+ ion, there is a lack of data in the low frequency region (several hundred cm^{-1}), in which the H_3O hindered rotation frequency (i.e. its torsional vibration frequency) could appear. Taylor and Vidale^{/5/} only suggest that the frequency 995 cm^{-1} may have the torsional vibration as its origin; however at the same time they write that this frequency is much too high for this type of vibration. On the other hand, a relatively narrow NMR line in the temperature region from 150°K to room temperature, with a broadening at lower temperatures, led Kakiuchi et al.^{/9/} to the suggestion that in perchloric acid monohydrate, starting from 150°K , the H_3O^+ rotation is relatively free. Neutron experiments, however, do not support this suggestion; the slope of the linear dependence between the total neutron scattering cross-section and the neutron wavelength is rather low ($8 \text{ b}/\text{\AA}$), which might be considered as an argument that the barrier to rotation is $\approx 1,8 \text{ kcal/mol}$ (J.M.Janik^{/13/}). Also the neutron spectrum obtained by the scattering of cold neutrons from a crystalline H_3OClO_4 (Janik et al.^{/12/}) shows a sharp peak, which could be interpreted as being caused by a torsional vibration of the group with a corresponding energy $\hbar\omega = 0,056 \text{ eV}$.

On the basis of the situation described above we decided to perform for NH_4ClO_4 and H_3OClO_4 additional neutron measurements, this time by applying a so-called "inverted geometry". The reason for this these experiments may be explained as follows. First - in the "inverted geometry" technique neutron energy losses (caused by the molecular degrees of freedom of the sample) are measured, whereas in the "normal geometry" neutron energy gains caused by excited energy levels of the sample are obtained. From this point of view, previous results^{/12/} may be compared to anti-Stokes lines in the Raman technique. It is interesting to support these results by obtaining the "Stokes-lines" characteristic for the "inverted geometry" technique. Second - the "inverted geometry" technique works much better than the "normal geometry" when applied to samples in lower temperatures. Therefore it was then possible to investigate the dynamics of NH_4 group in NH_4ClO_4 in a wide temperature interval: from liquid nitrogen to room temperature.

2. Experimental technique

The inverted beryllium filter arrangement constructed at the pulsed reactor IBR of the Joint Institute of Nuclear Research at Dubna was applied. A detailed description of the arrangement with an analysis of the resolution of the instru-

ment has been published elsewhere^{/17/}; at present only the main parameters of the apparatus will be given. In the pulsed reactor pulses of fast neutrons with a repetition ratio 8 pulses per second were produced. The duration of an impulse was $\approx 36 \mu\text{sec}$. Neutrons were slowed down in a moderator. This caused an increase in the pulse duration to $\approx 120 \mu\text{sec}$. Then, after passing a 20 m long flight path, the neutrons reached the sample, scattered under the 90° angle, and were transmitted through a nitrogen cooled Be-filter to a scintillation counter. In this arrangement the counter could register only neutrons whose wavelength was above the Be-cut-off i.e. neutrons of the most probable energy 3,7 meV. From the flight-path distances: moderator-sample (L_1), sample-detector (L_2), ($L_1 \gg L_2$) and the measured time distribution of neutrons arriving at the detector at the end of the flight-path, the incident neutron energy may be computed. In this way, for each incident neutron energy it was possible to measure the number of neutrons which in the scattering process obtained energy below the Be-cut-off.

Neutron spectra obtained in this way were however distorted in several narrow energy intervals because of the fact that, besides the main neutron pulses, some additional, much weaker neutron pulses were produced in the reactor with a 10 times greater repetition ratio. These fast neutron pulses naturally caused sharp peaks in periodic intervals of the time of flight scale i.e. in some narrow energy intervals of incident neutrons. The distorted parts of the spectrum were, of course, worthless for analysis of results and therefore in the corresponding plots experimental points were not plotted there and empty places were left.

Measurements for NH_4ClO_4 were made in a thin wall aluminium sample holder, placed in a cryostat. The measurement at 78°K was made with the cryostat filled with liquid nitrogen. Then, after the evaporation of the nitrogen, two hour measurement were performed at higher temperatures. Background measurements were made with a Cd shield in the beam of incident neutrons.

Measurements for H_3OClO_4 were performed in another aluminium sample holder with thicker (1 mm) walls. This was necessary because of a design solution which assured the hermetic sealing of the sample holder. Background measurements were made with an identical, empty sample holder replacing the sample.

The thicknesses of the two substances were sufficiently small to justify the neglect of the multiple scattering correction.

3. Results

Fig. 1 presents results for the crystalline NH_4ClO_4 in the temperature region from liquid nitrogen to room temperature. The values plotted are the differences $I_0 - I_{\text{back}}$ between the total number of observed counts and the background (without normalization to constant incident flux). Each plot shows an elastic part in the form of a beryllium cut-off and an inelastic part in the form of a broad distribution. All five plots are normalized to the same height of the inelastic part and pushed aside along the vertical axis with an arbitrary scale.

As the main result for NH_4ClO_4 we consider the fact one obtains in the inelastic part at all temperatures broad distributions without any sharp peaks. These distributions are after all identical. The elastic part decreases regularly with the temperature increase and is very weak at room temperature.

Fig. 2 presents the results obtained for the crystalline H_3OClO_4 at room temperature. In the same Fig. is shown for comparison the result for NH_4ClO_4 at room temperature. This other plot is normalized to the same height of the inelastic parts and pushed aside along the vertical axis with an arbitrary scale.

As the main result for H_3OClO_4 we consider the fact that the inelastic part shows a sharp peak at incident neutron energy 0,058 eV. The elastic part for H_3OClO_4 is much higher than for NH_4ClO_4 at the same temperature.

4. Discussion

The lack of sharp peaks in the neutron spectra obtained in whole temperature region for NH_4ClO_4 excludes the existence of torsional vibration levels and therefore supports the hypothesis of free rotation of NH_4 groups. This result agrees with the interpretation of data obtained by Richards and Schaefer^{/7/} by NMR method. It agrees also neutron investigations^{/10-12/}. As compared with the previous neutron measurements^{/12/} the present data are an essential extension because the measurements were carried out not only at room temperature but in a broad temperature region including liquid nitrogen temperature.

The result obtained for H_3OClO_4 at room temperature supports the interpretation of the previous neutron experiments^{/12,13/} which suggests hindered rotation of the H_3O groups. On the basis of the experimental data of the present work an attempt has been made to present them in a form independent from the neutron scattering dynamics but dependent only on the molecular dynamics of the substance. This was done by a transformation of data from a form in which the scattered

neutron intensity is presented in dependence on the incident neutron energy to a form $p_H(\epsilon)e^{-2W_H}$, where p_H is the frequency distribution of hydrogen atoms, $\epsilon = \hbar\omega$ corresponds to the neutron energy loss and e^{-2W_H} is the Debye-Waller factor. In this representation is also included normalization to a constant value of incident flux. It must be pointed out that if the torsional vibration peaks are not very sharp they will not appear in this representation in the same places as in the Fig. 2 representation. This explains why the value $\Delta E = \epsilon = 0,054\text{eV}$ obtained from Fig. 2, although being in agreement (within the limits of experimental errors) with $\Delta E = \epsilon = 0,056\text{ eV}$ obtained for a torsional vibration peak in H_3OClO_4 by Janik et al.^{/12/}, cannot be directly considered as $\hbar\omega_L$ (where ω_L is the frequency of torsional vibration). Fig. 3 presents the function $p_H(\epsilon)e^{-2W_H}$ for H_3OClO_4 calculated on the basis of the data of Fig. 2. This function has a maximum at $\epsilon = 0,062\text{ eV}$ which, according to our interpretation, should correspond to the energy $\hbar\omega_L$; this gives for $\omega_L = 497\text{ cm}^{-1}$.

It is worth while to note that the Raman frequency 995 cm^{-1} obtained by Taylor and Vidale^{/5/} was by them interpreted as ω_L . If, however, it is not ω_L but $2\omega_L$, one obtains for $\omega_L = 497\text{ cm}^{-1}$ in an excellent agreement with our results.

With regards to the suggestion of free rotation of H_3O groups in H_3OClO_4 made on the basis of the NMR measurements^{/7,9/}, it should be pointed out that a narrow resonance line cannot be treated simply as a proof of free rotation but only as evidence of a reorientation of the H_3O group which occurs with a frequency greater than $c_s \cdot 50\text{ kc/sec}$. This reorientation does not exclude the existence of a torsional vibration (with reorientational tunnel transitions).

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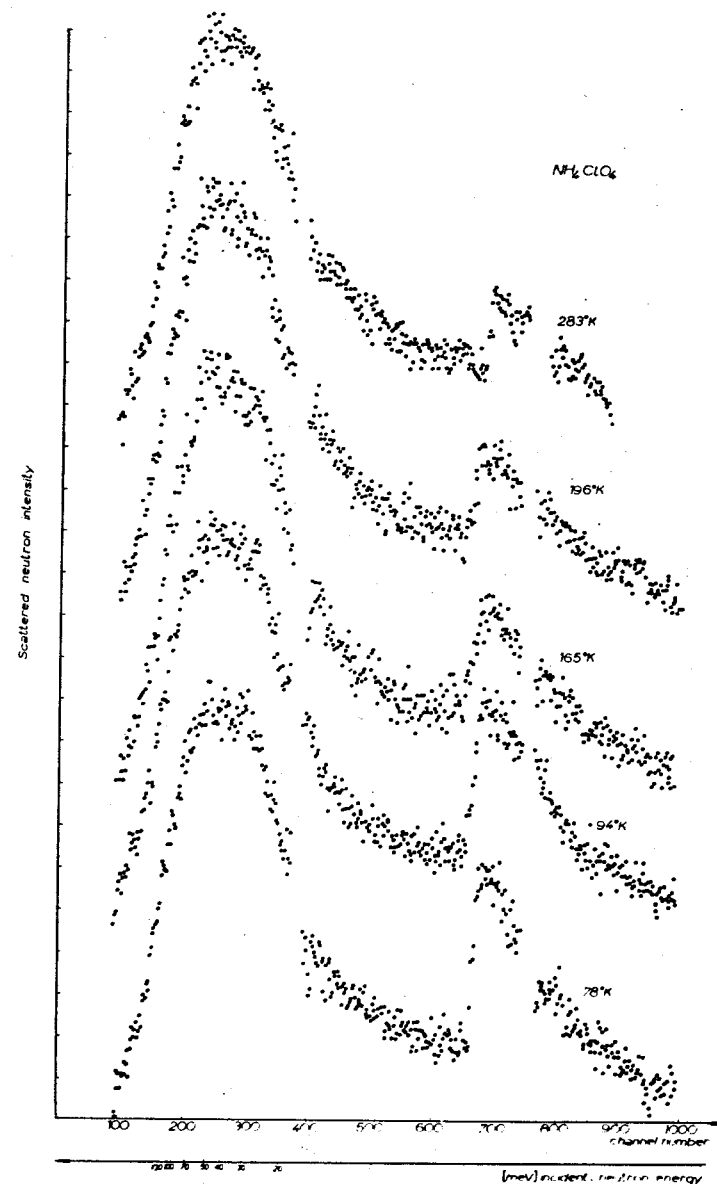


Fig. 1. The intensity of neutrons scattered by the crystalline NH_4ClO_4 vs. the incident neutron energy. Temperatures of the sample: 78°K , 94°K , 165°K , and 283°K . Scattering angle - 90° .

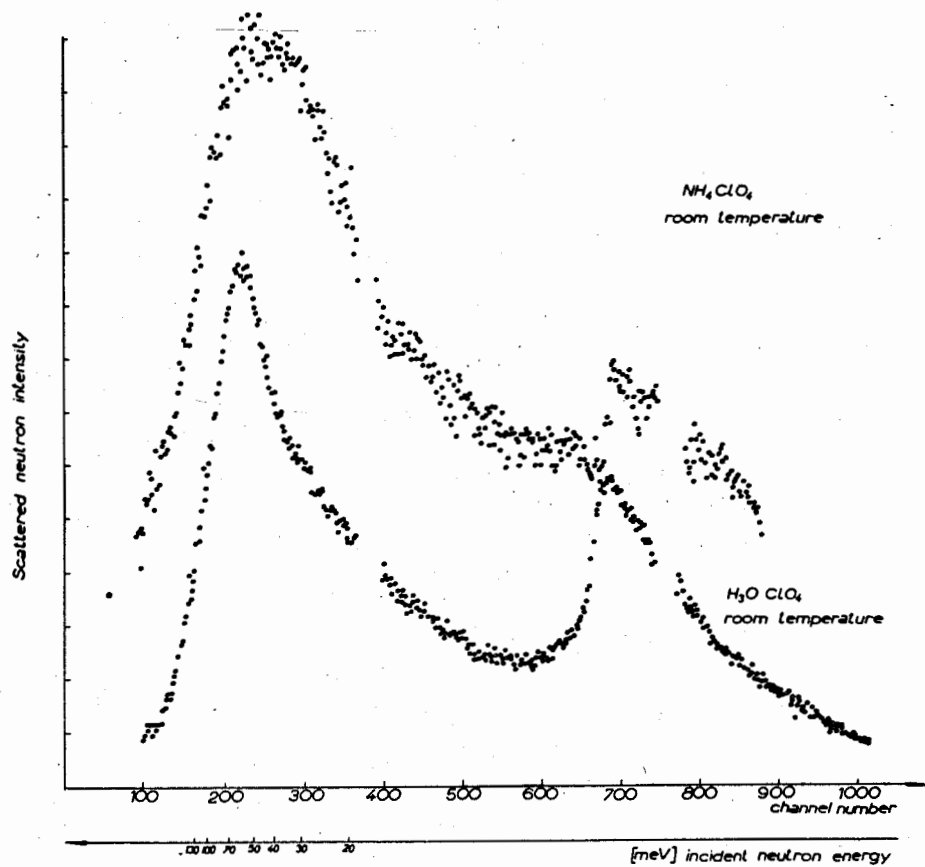


Fig. 2. The intensity of neutrons scattered by the crystalline NH_4ClO_4 and the crystalline H_3OClO_4 vs. the incident neutron energy. Both samples at room temperatures. Scattering angle - 90° .

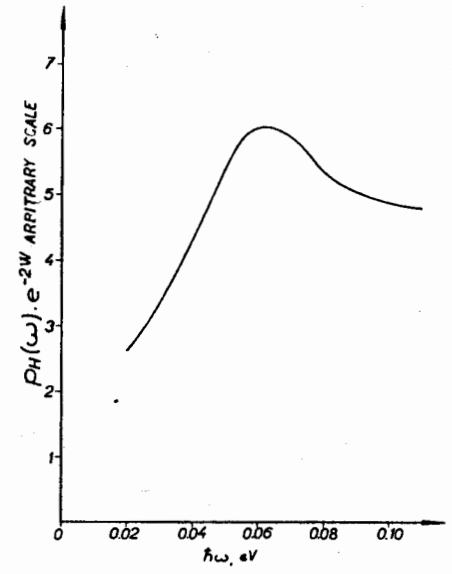


Fig. 3. Function $p_H(\omega) \cdot e^{-2W}$ for a crystalline H_3OClO_4 at room temperature.