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QUASIELASTIC NEUTRON SCATTERING  
AND INFRA-RED BAND CONTOUR STUDY  
OF H<sub>2</sub>O REORIENTATIONS  
IN  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$

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QUASIELASTIC NEUTRON SCATTERING AND INFRA-RED BAND CONTOUR  
STUDY OF H<sub>2</sub>O REORIENTATIONS IN [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>

BADANIA RUCHÓW REORIENTACYJNYCH MOLEKUL H<sub>2</sub>O W [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>  
METODĄ KWAZIELASTYCZNEGO ROZPRASZANIA NEUTRONÓW I METODĄ  
ANALIZY KONTURU PASMA W PODCZERWIENI

ИССЛЕДОВАНИЯ МЕТОДОМ КВАЗИУПРУГОГО РОССЕЯНИЯ НЕЙТРОНОВ  
И МЕТОДОМ АНАЛИЗА КОНТУРОВ ИНФРАКРАСНЫХ СПЕКТРОВ ДВИЖЕНИЯ  
МОЛЕКУЛ H<sub>2</sub>O В [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>

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**Wydanie I**

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IR band contour measurements carried out for  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  revealed an existence of fast  $\text{H}_2\text{O}$   $180^\circ$  flips around Ni-O axes at room temperatures. These flips were subjected to a more accurate study by the quasielastic neutron scattering method. Correlation times of the order of picosecond were obtained for room temperatures and the barrier to rotation of ca. 7 kcal/mole. The results are compared to those previously obtained for  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  and also to those for  $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$  and  $[\text{Mg}(\text{NH}_3)_6](\text{ClO}_4)_2$ .

Analiza profilu pasma podczerwonego dla  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  ujawniła istnienie szybkich przeskoków molekuł  $\text{H}_2\text{O}$  wokół osi Ni-O o kąt  $180^\circ$  w temperaturze pokojowej. Te przeskoki były również przedmiotem bardziej dokładnych badań metodą kwazi-elastycznego rozpraszania neutronów. Wyznaczony w temperaturze pokojowej czas korelacji jest rzędu pikosekund, a bariera hamująca rotację wynosi około 7 kcal/mol. Wyniki porównano z wynikami otrzymanymi uprzednio dla  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  oraz  $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$  i  $[\text{Mg}(\text{NH}_3)_6](\text{ClO}_4)_2$ .

Анализ контура инфракрасного максимума для  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  показал существование в комнатной температуре быстрых перепрыжков молекул  $\text{H}_2\text{O}$  вокруг оси Ni-O на  $180^\circ$ . Эти перепрыжки были тоже предметом более точных исследований проведенных методом квазупругого рассеяния нейтронов. Определено в комнатной температуре время корреляции порядка пикосекунд, а барьер тормозящий ротацию около 7 ккал/мол. Результаты сравнено с результатами полученными прежде для  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ ,  $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$  и  $[\text{Mg}(\text{NH}_3)_6](\text{ClO}_4)_2$ .

## 1. INTRODUCTION

Several experimental techniques have been applied with an aim to get information on phase transitions and molecular dynamics in two isomorphous compounds  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  and  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ .

Both compounds, studied by the adiabatic calorimetry, revealed specific heat anomalies: at 361 K and 311 K for the nickel compound and at 325 K and 273 K for the magnesium compound [1,2]. In both compounds, Raman contour studies led to a conclusion that there exists a high reorientational mobility of  $\text{ClO}_4^-$  ions in the high temperature phase and a slowing down of this mobility at the phase transition: at 361 K for the nickel compound and at 325 for the magnesium compound [3].

What concerns the  $\text{H}_2\text{O}$  reorientational mobility around the metal-oxygen axes, an extensive study exists for  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  [4]. Reorientational  $180^\circ$   $\text{H}_2\text{O}$ -flips were discovered in this study and a perfect agreement between the two methods applied: the proton magnetic relaxation and the neutron quasi-elastic scattering, was obtained. Moreover, these  $\text{H}_2\text{O}$ -flips seemed to be not significantly affected by the phase transitions at 325 K and 273 K.

The aim of the present study is to present similar information concerning the  $\text{H}_2\text{O}$  motions for  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ . This information was obtained mainly from the quasielastic neutron scattering (QNS), as the NMR measurements are impossible for the nickel substance. However, we present as a qualitative check, results of the IR band contour study.

## 2. INFRA-RED MEASUREMENTS

The IR measurements for polycrystalline  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  were carried out on the Zeiss UR 20 spectrometer in the temperature range 100 K - 365 K. The  $\delta(\text{HDE})\text{A}$  band at  $1620 \text{ cm}^{-1}$  was chosen for analysis. A Lorentz function was fitted to the band contour. The width of this function at the half maxima (FWHM) was considered as carrying information concerning  $\text{H}_2\text{O}$  reorien-

tations. No instrumental width correction was made, as the FWHM of the band appeared to be ca. one order of magnitude larger than the spectral width.

Fig. 1 presents the peak intensity of the band vs. temperature. Fig. 2 shows the FWHM of the band vs. temperature. The strong temperature dependence at higher temperatures is believed as caused mainly by the H<sub>2</sub>O reorientational flips, which die out when the temperature lowers, leaving only the vibrational relaxation component at low temperatures. The H<sub>2</sub>O flips in the high temperature region must occur in the picosecond correlation time region, but nothing more accurate can

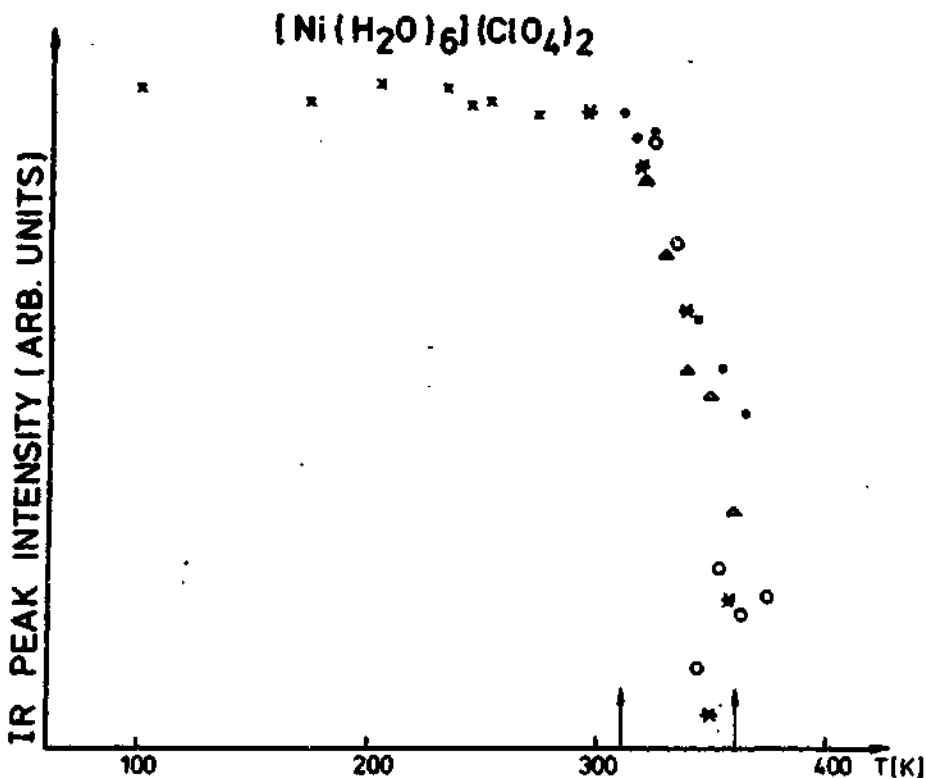


Fig. 1. Peak intensity of the  $1620 \text{ cm}^{-1}$  IR band vs temperature. Arrows show the phase transition points. Various points (x, \*, ., Δ, o) correspond to different experimental runs.

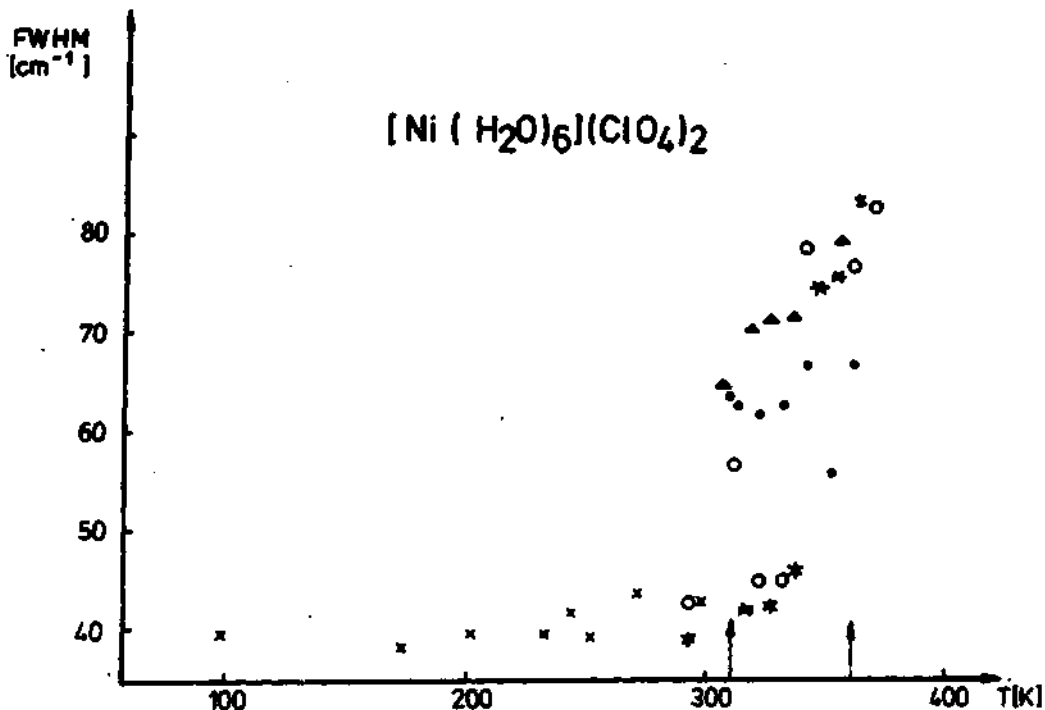


Fig. 2. FWHM of  $1620 \text{ cm}^{-1}$  IR band vs temperature. Arrows show the phase transition points. Various points ( $\times$ ,  $*$ ,  $\cdot$ ,  $\Delta$ ,  $\circ$ ) correspond to different experimental runs.

be said, because we have no possibility of evolution of the vibrational relaxation component contribution at higher temperatures. Therefore much more accurate QNS measurements were carried out and they are presented in the next Sec.

### 3. INCOHERENT QUASIELASTIC NEUTRON SCATTERING MEASUREMENTS

The QNS measurements were carried out at the JEEP II reactor of the Institutt for Energiteknikk at Kjeller, Norway, by applying the time-of-flight spectrometer cooperating with the cold neutron source. Experimental conditions were exactly the same as those described in [4] in connection with the  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  measurements.

The measurements were made in following temperatures: 363 K, 342 K, 323 K, 304 K, 296 K, 272 K, 233 K, 227 K, 213 K and ca. 253 K. The instrumental energy resolution was 0.172 meV for temperatures  $\geq 296$  K; for the lower temperatures it amounted to 0.162 meV. No multiple scattering correction was made.

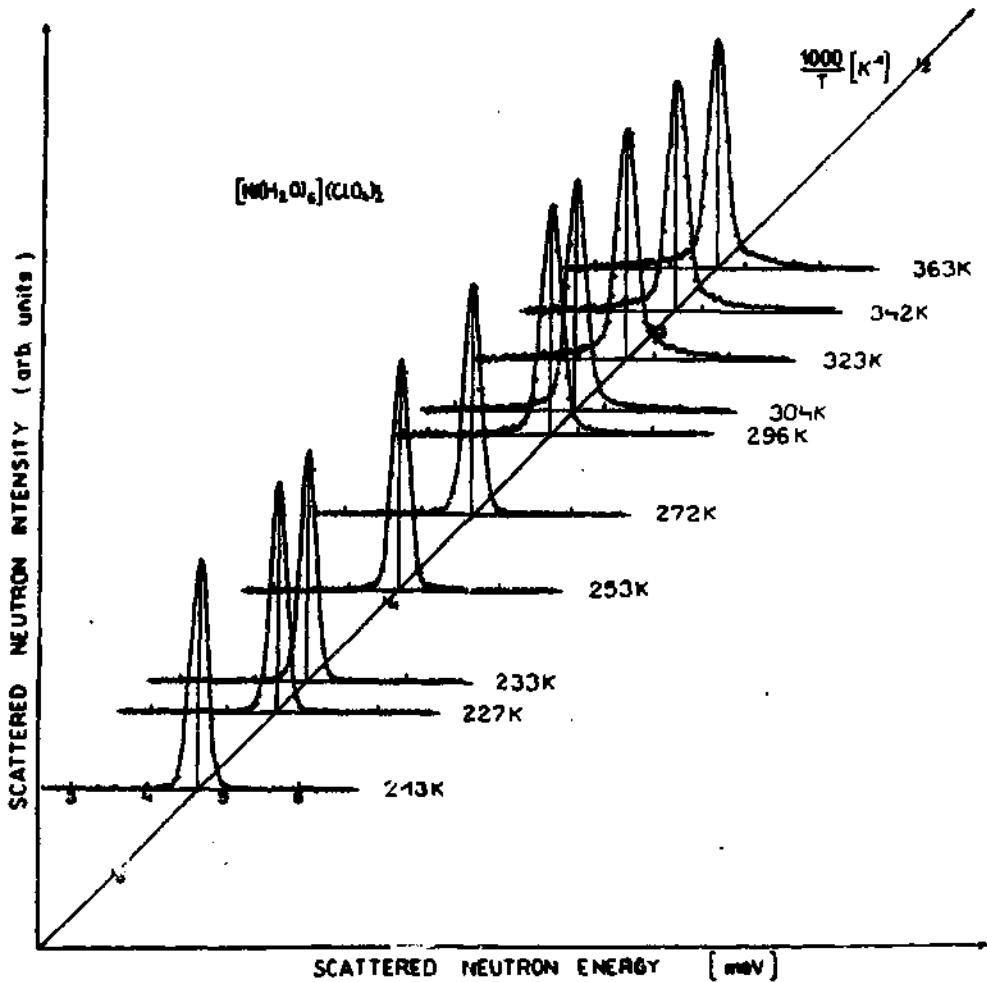
The QNS results were transformed from the wavelength to the energy scale. In this scale the background was subtracted as a straight line connecting the far lying points of the wings. To the so obtained QNS peak the model scattering function convoluted by the Gaussian instrumental function was fitted by the computer.

Like for  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ , the instantaneous  $180^\circ$   $\text{H}_2\text{O}$  flips around the metal-oxygen axis were chosen as the reorientational model. The respective formulas are given in [4]. From the fittings, the average times  $\tau$  between instantaneous angular jumps were obtained for each temperature. The  $\chi^2$  values were also obtained and served as a test of the quality of the fits.

Fig. 3 present, for ten chosen temperatures, the examples of the experimental QNS peaks and the model fits. Fig. 4 shows the average time  $\tau$  values vs. temperature. It is evident that the  $\tau$  values are indeed of the order of picoseconds for temperatures from the room temperature range. The barrier to  $\text{H}_2\text{O}$  reorientation is quite high, 7 kcal/mole, so that the reorientations slow down quickly with the decreasing temperature, and become invisible by the QNS method below ca. 250 K. There is no reason to speculate about any significant perturbation of  $\text{H}_2\text{O}$  flips by the phase transition, similar to the case of  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  substance.

As compared to the  $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  substance the barrier for  $\text{H}_2\text{O}$  flips in  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  is considerably higher (for magnesium compound it amounted to 3.2 kcal/mole and hence the  $\tau$  values are larger when compared at the same temperatures.





**Fig. 3.** Experimental QNS peaks together with the model curves (solid lines) obtained by fitting to the experimental points ( $\bullet$ ). Scattering angle  $80^\circ$ .

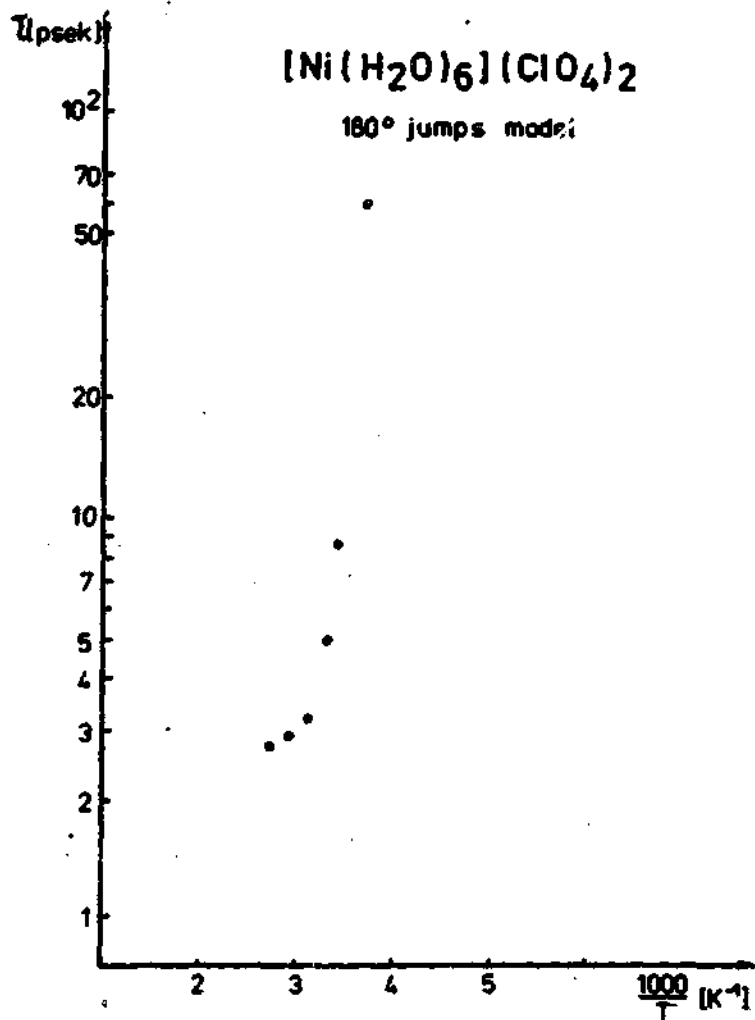


Fig. 4. Average times between instantaneous angular 180° H<sub>2</sub>O jumps vs 1000/T, as obtained from the QNS measurements

#### 4. CONCLUSIONS

1.  $H_2O$  groups in  $[Ni(H_2O)_6](ClO_4)_2$  perform uniaxial reorientations around Ni-O axes, probably via  $180^\circ$  angular flips.

2. At room temperatures the correlation times for this motion are of the order of several picoseconds. These correlation times become larger at lower temperatures in agreement with a relatively high barrier ca. 7 kcal/mole.

3. There is no indication that the  $H_2O$  flips are perturbed by the phase transitions at 311 K and 361 K.

4.  $H_2O$  motions, as well as  $ClO_4^-$  motions [3], in  $[Ni(H_2O)_6](ClO_4)_2$  are qualitatively similar to those in  $[Mg(H_2O)_6](ClO_4)_2$  studied in [4]. The barrier to  $H_2O$  flips in  $[Mg(H_2O)_6](ClO_4)_2$  is, however, considerably lower (3,2 kcal/mole).

5.  $H_2O$  flips in both substances have significantly higher barriers as compared to  $[Ni(NH_3)_6](ClO_4)_2$  and  $[Mg(NH_3)_6](ClO_4)_2$  where it amounts to ca. 0.5 kcal/mole [5],[6].

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## REFERENCES

- [1] M.Rachwalska, T.Stanek, Phys. Stat. Sol.(a) 48, 297 (1978).
- [2] E.Mikuli, A.Migdał-Mikuli, M.Rachwalska, T.Stanek, Physica, in press.
- [3] J.M.Janik, A.Migdał-Mikuli, E.Mikuli, T.Stanek, Acta Phys. Polon., in press.
- [4] I.Svare, B.O.Finland, K.Otnes, J.A.Janik, J.M.Janik, E.Mikuli, A.Migdał-Mikuli, Physica, in press.
- [5] J.A.Janik, J.M.Janik, K.Otnes, K.Rościszewski, Physica 93B, 259 (1976).
- [6] J.A.Janik, J.M.Janik, A.Migdał-Mikuli, E.Mikuli, K.Otnes, I.Svare, Physica 97B, 47 (1979).

