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A. Bajorek , J.M. Janik, , J.A. Janik,  
K. Parliński, M. Sudnik-Hryniewicz

MOLECULAR DYNAMICS STUDY BY THE  
NEUTRON INELASTIC SCATTERING  
METHOD III. NITRIC ACID MONOHYDRATE

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A. Bajorek\*\*, J.M. Janik, \*, J.A. Janik,  
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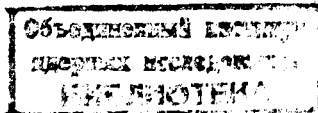
**MOLECULAR DYNAMICS STUDY BY THE  
NEUTRON INELASTIC SCATTERING  
METHOD III. NITRIC ACID MONOHYDRATE**

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<sup>x/</sup>Laboratory of Physical Chemistry and Electrochemistry of the Jagiellonian University, Krakow.

<sup>xx/</sup>Laboratory of Structure Research of the Jagiellonian University, Krakow.



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## I. Introduction

The structure of the crystalline nitric acid monohydrate was studied by X-ray diffraction by Luzzati<sup>/1/</sup>. He demonstrated that solid monohydrate has an orthorhombic structure, belonging to the space group  $C_{2v}$ . In this structure there are layers of plane  $\text{NO}_3^-$ -ions situated alternately with layers of  $\text{H}_3\text{O}^+$ -ions. Luzzati interpreted his results on the basis of the chemical formula  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ , whereas nowadays a formula  $\text{H}_3\text{O}^+ \cdot \text{NO}_3^-$  is generally accepted. There is no doubt, however, that the positions determined for O and N atoms are in his study correct.

Richards and Smith<sup>/2/</sup> studied the crystalline nitric acid monohydrate by the MNR method. Their results may be considered as a proof of the existence of the hydronium ion ( $\text{H}_3\text{O}^+$ ) in crystalline monohydrate, which leads to the chemical formula  $\text{H}_3\text{O}^+ \cdot \text{NO}_3^-$ .

There are strong arguments<sup>/3/</sup> supporting the statement that in liquid monohydrate, on the other hand, there are no  $\text{H}_3\text{O}^+$ -ions, but only molecules of undissociated acid ( $\text{HNO}_3$ ) and water ( $\text{H}_2\text{O}$ ).

Information concerning the dynamics in crystalline monohydrate was obtained by Bethell and Sheppard<sup>/4,5/</sup> and by Savcic and Giguère<sup>/6/</sup> by infra-red absorption. Bethell and Sheppard measured the absorption spectrum in a wave number region of  $550 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$  and Giguère in a region of  $100 \text{ cm}^{-1} - 3000 \text{ cm}^{-1}$ . In both works the spectra were measured in a temperature close to that of liquid nitrogen, and in the former one, also in liquid monohydrate. It was shown that the spectrum of liquid substance is similar to that of pure  $\text{HNO}_3$ , but with an additional band interpreted as being caused by  $\text{H}_2\text{O}$ -molecules. This result supports the statement that liquid monohydrate of nitric acid is unionized. For crystal-

line monohydrate the two works gave spectra which were interpreted either as internal vibrations of  $\text{NO}_3^-$  and  $\text{H}_3\text{O}^+$  ions (for wave numbers above  $700 \text{ cm}^{-1}$ ), or as lattice vibrations i.e. translational and torsional vibrations of the  $\text{H}_3\text{O}^+$ -group (below  $700 \text{ cm}^{-1}$ ). That is to say, the bands obtained by Savoie and Giguère at  $117 \text{ cm}^{-1}$ ,  $205 \text{ cm}^{-1}$ , and  $237 \text{ cm}^{-1}$  were interpreted as translational vibration of  $\text{H}_3\text{O}^+$ -group ( $T_x, T_x, T_y$  respectively) and the band at ca.  $670 \text{ cm}^{-1}$ , observed in both works, was interpreted as torsion of the  $\text{H}_3\text{O}^+$ -group ( $R_x, R_y$ ).

In this situation it seemed interesting to investigate the nitric acid monohydrate by the neutron inelastic scattering method in a wide temperature interval covering solid and liquid phases. The selective sensitivity for hydrogen of the neutron scattering cross-section leads to the possibility of selecting those vibrations in which hydrogen takes part. It should also be pointed out that the INS method gives information concerning frequency distribution for all  $q$ -values<sup>[7]</sup> ( $q$  is the wave number of a phonon representing a given vibration), thus it is complementary to spectroscopic methods whose correspond to the region near  $q = 0$  only<sup>[8]</sup>.

## 2. Experimental Technique

The nitric acid monohydrate was obtained by dilution of concentrated  $\text{HNO}_3$  to a solution which corresponded to a stoichiometric ratio of  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ , determined by titration.

Especially difficult was the sampleholder problem, owing to the strong chemical activity of the substance. The aluminium sampleholders normally used in such measurements were replaced by a layer of ca. 130 glass tubes (ext. diameter ca. 0.9 mm, int. diameter ca. 0.5 mm), which were filled in vacuum with nitric acid monohydrate and sealed at both ends. The total area of the layer of tubes was  $15 \times 15 \text{ cm}^2$ . A similar layer of empty glass tubes was also made for determination of the background caused by the scattering of neutrons from the glass walls of the tubes. The two layers were mounted on both sides of a cadmium plate. The construction of sampleholders described as above made impossible the occurrence of any chemical changes in the sample during the measurement, although it caused a considerable decrease of the effect.

The whole system (the two layers of tubes on each side of a Cd plate) was placed in the cryostat described by Sudnik-Hryniewicz et al.<sup>[9]</sup>.

The cryostat permitted the performance of measurements at any temperature in a region from  $-150^{\circ}\text{C}$  to room temperature. The measurements with the nitric acid monohydrate were made at temperatures:  $-150^{\circ}\text{C}$ ,  $-100^{\circ}\text{C}$ ,  $-50^{\circ}\text{C}$ ,  $-30^{\circ}\text{C}$  and  $+23^{\circ}\text{C}$  (the monohydrate melted at  $-38^{\circ}\text{C}$ ).

It should be pointed out that the nitric acid monohydrate may be easily supercooled to glass form. For instance, this fact was observed in the experiments of Richards and Smith<sup>[2]</sup>. In our preliminary tests of the glass tubes with the substance, i.e. those connected with verification of the melting point, this effect of supercooling was also observed, even at very low temperature of ca.  $-150^{\circ}\text{C}$ .

The measurements of inelastic neutron scattering were carried out using a time of flight neutron spectrometer with Be-filter in front of detector described in<sup>[10]</sup>.

### 3. Experimental Results

Figs 1 and 2 present the results (in the two Representations described in Part 1) obtained for the crystalline nitric acid monohydrate at temperatures  $-150^{\circ}\text{C}$ ,  $-100^{\circ}\text{C}$  and  $-50^{\circ}\text{C}$  and those obtained for the liquid monohydrate at  $-30^{\circ}\text{C}$  and  $+23^{\circ}\text{C}$ .

In crystalline monohydrate at  $-150^{\circ}\text{C}$  there is a strong peak corresponding to a frequency of  $847\text{ cm}^{-1}$ , then a weaker one at  $228\text{ cm}^{-1}$ , there being also a weak, diffuse band at still lower frequencies. The situation at temperatures  $-100^{\circ}\text{C}$  and  $-50^{\circ}\text{C}$  is similar. The  $847\text{ cm}^{-1}$  peak does not show any temperature dependence (apart from some broadening), whereas the other peak shifts to somewhat lower frequencies ( $222\text{ cm}^{-1}$  at  $-100^{\circ}\text{C}$  and  $215\text{ cm}^{-1}$  at  $-50^{\circ}\text{C}$ ).

The results obtained for the liquid monohydrate are entirely different. There is a strong, broad band with a maximum at ca.  $600\text{ cm}^{-1}$ , weak peaks at ca.  $140\text{ cm}^{-1}$  and  $190\text{ cm}^{-1}$ , and diffuse traces of other weak peaks at still lower frequencies. One may also observe for liquid monohydrate a broadening of the beryllium cut-off i.e. of the spectrum of

quasi-elastically scattered neutrons. This broadening proves that there is diffusion in the liquid phase.

It should be pointed out that the procedure of obtaining the results was as follows: After placing the sample in the cryostat it was cooled from room temperature to  $-150^{\circ}\text{C}$  during approximately three hours. The measurement at this temperature was then made. The result was entirely different from those presented above for crystalline substance but it was very similar to those corresponding to liquid monohydrate. The main difference was in the shape of the Be-cut-off which was not broadened, this meaning that there is no diffusion in the substance. Afterwards the measurements at  $-100^{\circ}\text{C}$  and  $-50^{\circ}\text{C}$  were made, the results obtained being shown in Figs. 1 and 2 for two temperatures. The temperature  $-150^{\circ}\text{C}$  was then adjusted once more the result obtained being given in Figs. 1 and 2 (the lowest curve). No doubt, the first result for  $-150^{\circ}\text{C}$  corresponds to the supercooled glass form and the results obtained afterwards for  $-100^{\circ}\text{C}$ ,  $-50^{\circ}\text{C}$ , and  $-150^{\circ}\text{C}$  are for the crystalline substance. Fig. 3 presents the results for the glass form of the monohydrate at  $-150^{\circ}\text{C}$ . For comparison the curve for liquid substance at  $-30^{\circ}\text{C}$  taken from Fig. 1 is also shown.

#### 4 Discussion

It seems reasonable to state that peak at  $228\text{ cm}^{-1}$  obtained for the crystalline monohydrate at  $-150^{\circ}\text{C}$  is the same band as that observed by Savoie and Giguère <sup>[6]</sup> in infra-red absorption in the form of two peaks at  $237\text{ cm}^{-1}$  and  $205\text{ cm}^{-1}$ . (It should be mentioned here that the resolution of the neutron method is lower than that attainable by spectroscopy). The weak band observed by us at a still lower frequency is probably the same as that of Savoie and Giguère at  $117\text{ cm}^{-1}$ . The interpretation given by these authors (translational vibrations of  $\text{H}_3\text{O}^+$ -ions) also seemed correct. It should be mentioned that vibrations of this kind cause deformation and stretching of hydrogen bonds in the crystal.

The intense peak at  $847\text{ cm}^{-1}$  observed by us is no doubt caused by a vibration in which hydrogen atoms play some role. We consider

that this peak should be interpreted as being caused by torsional vibration of the  $H_3O^+$ -group. In spectroscopic works<sup>/5,6/</sup>, on the other hand, the frequency at  $670\text{ cm}^{-1}$  was interpreted as corresponding to the torsional motion of the  $H_3O$ -group. This peak was not observed in the neutron spectrum. The only explanation of this disagreement involves the assumption that the optical branch of dispersion relation of phonons representing this torsional vibration has a strong dispersion i.e. it is a relatively strongly increasing function with  $q$ -values increasing from zero to the end of Brillouin zone<sup>x/</sup>. It should be pointed out here that an agreement between spectroscopic and neutron data may be expected only when the corresponding phonon branches have a very small dispersion. If the dispersion is large, then spectroscopy, whose frequencies correspond to the vicinity of  $q = 0$ , must give different results from those obtained by neutrons, which come from the whole region of  $q$ -s.

It is also worth while to mention that in spectroscopic works<sup>/5,6/</sup> a frequency of  $815\text{ cm}^{-1}$  was observed. This frequency is much closer to our value  $847\text{ cm}^{-1}$ , so that if it were possible to interpret it as torsion it would lead to a much flatter dispersion curve for this kind of vibration. However, the vibration at  $815\text{ cm}^{-1}$  was interpreted by the authors as being caused by  $NO_3^-$ -ion.

The results obtained in this work for the crystalline nitric acid monohydrate together with the previous spectroscopic results<sup>/5,6/</sup> and with an interpretation are assembled in Table 1.

The results obtained by us for the glass form of the monohydrate and for the liquid monohydrate are very similar to those of several authors for water<sup>/11-14/</sup>. The INS spectrum of water possesses a broad and intense band at ca.  $600\text{ cm}^{-1}$ , which is interpreted as caused by hindered rotation (torsion) of the  $H_2O$ -molecules. Apart from this, the spectrum shows translational bands at lower frequencies whose intensities are similar to those for liquid and supercooled monohydrate. Hence, it seems reasonable to interpret our results as supporting the statement that the hydronium ion does not exist in the liquid and glass form. The peaks observed in our INS spectrum for these phases are caused, then by  $H_2O$ -groups performing librations of the frequency ca.  $600\text{ cm}^{-1}$  and transla-

<sup>x/</sup> Additional support for this assumption is that the width of the  $847\text{ cm}^{-1}$ -peak is somewhat greater than that caused by resolution.

Table I

Frequencies observed for crystalline nitric acid monohydrate by the infra-red absorption method and by the neutron inelastic scattering method (frequencies below  $1000\text{ cm}^{-1}$ )

Bethell and Sheppard <sup>/5/</sup> Temp.-180°C /cm <sup>-1</sup> /	Savoie and Giguère <sup>/6/</sup> Temp.-180°C/cm <sup>-1</sup> /	This work Temp.-150°C /cm <sup>-1</sup> /	Interpre- tation
	117	weak diffuse band at several tens cm <sup>-1</sup>	H <sub>2</sub> O; T <sub>z</sub>
	205		
	237	228	H <sub>2</sub> O; T <sub>x</sub> , T <sub>y</sub>
	(239)?		
670	675	847	H <sub>2</sub> O; torsion
	700		
/723/	723		
738	737		
774	779		
816	815		
957	930		

tional vibrations with frequencies ca.  $140\text{ cm}^{-1}$  and  $190\text{ cm}^{-1}$ . This interpretation is in agreement with the assumption of a lack of dissociation of the liquid monohydrate suggested by Redlich and Bigeleisen<sup>/3/</sup> and Bethell and Sheppard<sup>/5/</sup>.

We are planning to repeat the INS measurements for nitric acid monohydrate by applying the Be<sup>-</sup> filter cooperating with a Zn<sup>-</sup> monocrystal technique, this method has a better resolution than the classical Be<sup>-</sup> filter one.

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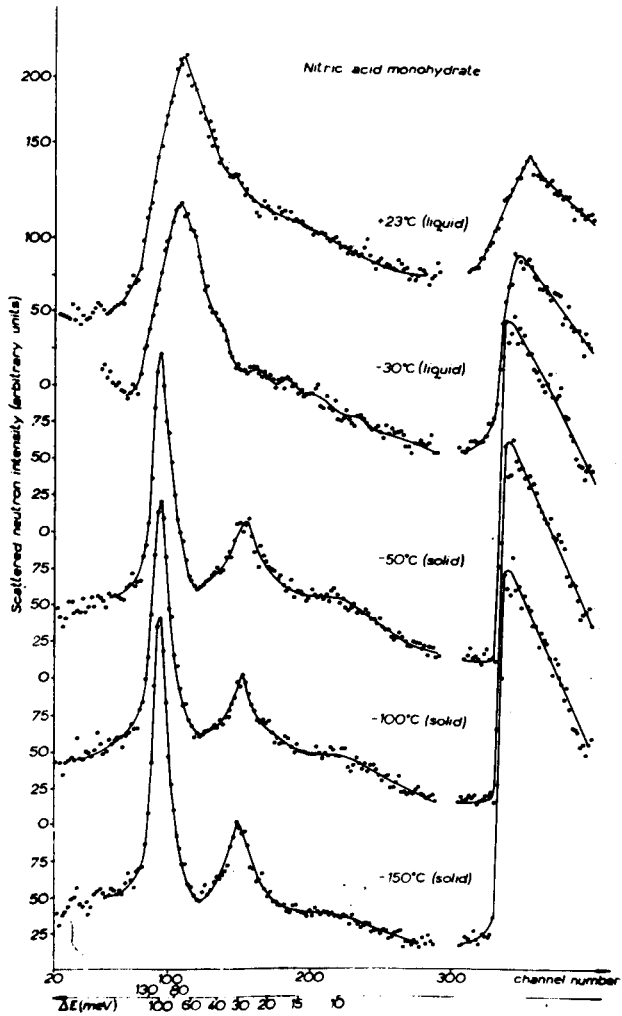


Fig. 1. The intensity of neutrons scattered from nitric acid monohydrate, at various temperatures, as a function of the analyser channel number. Channel width  $64 \mu \text{ sec}$ . The lower scale gives the energy transfer for inelastically scattered neutrons.

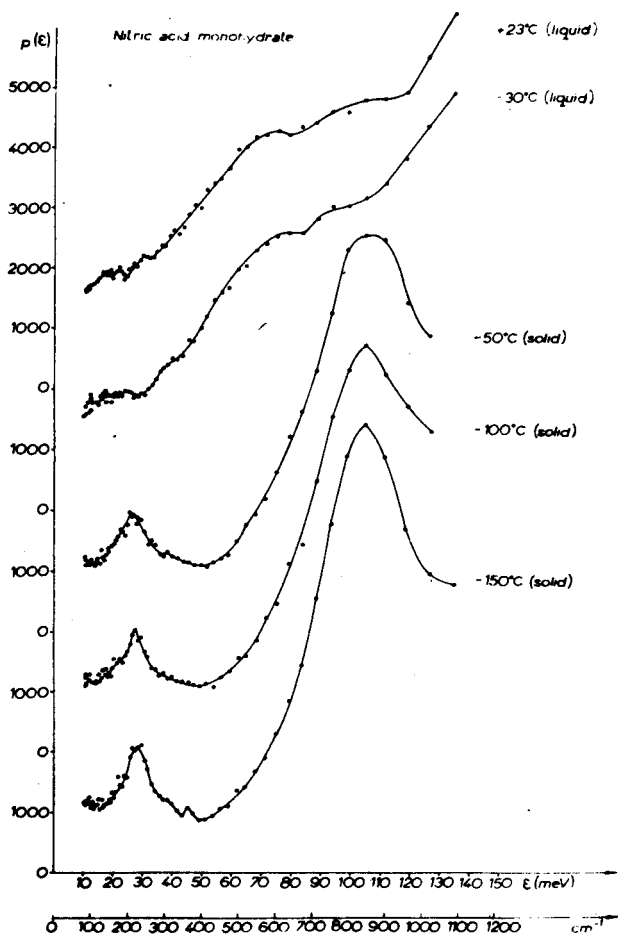


Fig. 2. The  $p(\epsilon)$  function for nitric acid monohydrate, at various temperatures.

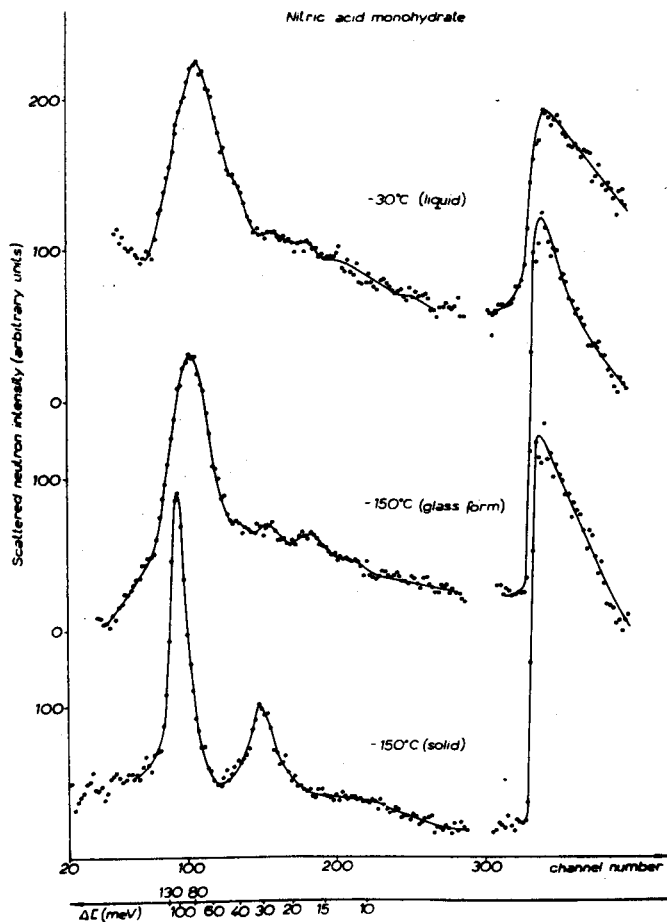


Fig. 3. A comparison of intensity distributions of neutrons scattered from crystalline, supercooled, and liquid nitric acid monohydrate. Explanations as in Fig. 1.