

LATTICE-MOLECULAR VIBRATIONS IN COMPLEXES:  $\text{Co}(\text{NH}_3)_6\text{I}_2$   
AND  $\text{Ni}(\text{NH}_3)_6\text{I}_2$ 

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Neutron incoherent inelastic scattering was measured for  $\text{Co}(\text{NH}_3)_6\text{I}_2$  and  $\text{Ni}(\text{NH}_3)_6\text{I}_2$ . Three peaks were obtained in a region below  $300\text{ cm}^{-1}$ : at  $70\text{--}80\text{ cm}^{-1}$  interpreted as  $\text{NH}_3$ -torsion, at  $100\text{--}110\text{ cm}^{-1}$  interpreted as optic translatory vibration, and at  $180\text{--}200\text{ cm}^{-1}$  interpreted as N—Me—N deformation vibration.

## 1. Introduction

Vibrations in crystalline complex compounds of the type  $\text{Me}(\text{NH}_3)_6^{3+}$  and  $\text{Me}(\text{NH}_3)_6^{2+}$  were the subject of many spectroscopy works. There is, however, insufficient information concerning the low energy part (below  $300\text{ cm}^{-1}$ ) of the vibrational spectrum. Some years ago Van Kempen *et al.* [1] measured the specific heat of some  $\text{Me}(\text{NH}_3)_6^{2+}$  compounds at temperatures below  $1^\circ\text{K}$  and obtained evidence of torsional motions of  $\text{NH}_3$  groups in  $\text{Me}(\text{NH}_3)_6$  octaheders. This evidence was obtained by observing specific heat anomalies caused by tunnelling splitting of  $\text{NH}_3$  torsional levels, which led to the determination of barrier-to-rotation height. From this height the torsional frequency could be determined. The thus obtained torsional frequencies for  $\text{Co}(\text{NH}_3)_6\text{I}_2$  and  $\text{Ni}(\text{NH}_3)_6\text{I}_2$  were (when expressed in  $\text{cm}^{-1}$ )  $81\text{ cm}^{-1}$  and  $79\text{ cm}^{-1}$  respectively.

A far infra-red investigation of  $\text{Me}(\text{NH}_3)_6^{2+}$  and  $\text{Me}(\text{NH}_3)_6^{3+}$  compounds was made by Sacconi *et al.* [2] at room temperature, in which they obtained for  $\text{Ni}(\text{NH}_3)_6\text{I}_2$  a peak at  $81\text{ cm}^{-1}$ , interpreted as optic translatory vibration of the complex ion octaheders against the iodine ions. Another peak obtained in [2] at  $216\text{ cm}^{-1}$  was interpreted as a frequency corresponding to N—Ni—N deformation.

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A neutron incoherent inelastic scattering (IINS) study performed for  $\text{Co}(\text{NH}_3)_6\cdot\text{I}_2$  and  $\text{Co}(\text{NH}_3)_6\cdot\text{I}_3$  by Jakó**o**b *et al.* [3] gave in the same frequency region, at a temperature 123°K, two very badly resolved peaks for  $\text{Co}(\text{NH}_3)_6\cdot\text{I}_2$ : at *ca.* 120  $\text{cm}^{-1}$  and at *ca.* 210  $\text{cm}^{-1}$ .

This situation, as described above, seems to be confusing in view of the following points:

1. Should or should not a coincidence between a far IR peak at 81  $\text{cm}^{-1}$  and a calorimetrically determined one at 79  $\text{cm}^{-1}$  [2], [1] for  $\text{Ni}(\text{NH}_3)_6\cdot\text{I}_2$  be treated as significant? There is a temptation to consider the two peaks as being caused by the same physical phenomenon and therefore to correct either the interpretation of paper [1] or that given in paper [2]. One should remember, however, that the "calorimetric" interpretation cannot be valid for the infra-red case and *vice versa*. Indeed, if we accept the "calorimetric" point of view and treat the specific heat anomaly below 1°K as being caused by  $\text{NH}_3$ -torsion, we must immediately notice that peaks corresponding to such motion are forbidden in IR. If, on the other hand, we accept the "far infra-red" point of view and consider the peak as being connected with optic translatory vibration, we must admit that there is no understanding why such motion should lead to a tunnelling splitting type of specific heat anomaly.

2. The IINS peak at *ca.* 120  $\text{cm}^{-1}$  obtained for  $\text{Co}(\text{NH}_3)_6\cdot\text{I}_2$  does not agree with that determined calorimetrically at 81  $\text{cm}^{-1}$  [3], [1], although the torsional motion (as well as optic translatory vibration) should be visible in neutron experiments.

Taking this situation into account, an attempt was made in the present work to present IINS data improved in resolution as compared with the data of paper [3]. Because of a simpler interpretation of optic translatory peaks, which is expected for  $\text{Me}(\text{NH}_3)_6^{2+}$  compounds as compared with  $\text{Me}(\text{NH}_3)_6^{3+}$  ones, we limited ourselves to the two substances:  $\text{Co}(\text{NH}_3)_6\cdot\text{I}_2$  and  $\text{Ni}(\text{NH}_3)_6\cdot\text{I}_2$ .

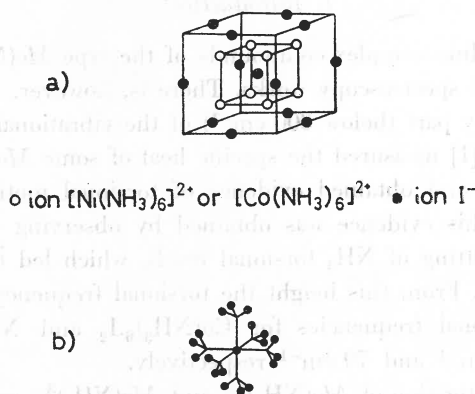


Fig. 1. a) Crystal structure of  $\text{Me}(\text{NH}_3)_6\cdot\text{I}_2$  complexes [6]. b) Structure of  $\text{Me}(\text{NH}_3)_6^{2+}$ -ion

The structure of the two crystal complexes is shown in Fig. 1. Both compounds belong to the space group  $O_h^5$ . The Bravais elementary cell contains 27 atoms: the complex ion  $\text{Me}(\text{NH}_3)_6^{2+}$  and two iodine ions.

Fig. 2 presents the two kinds of motions involved in the discussion: (a) torsional motion of  $\text{NH}_3$  groups and (b) optic translatory vibrations.

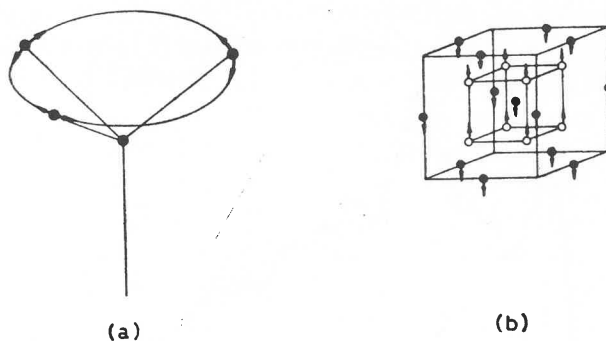


Fig. 2. a)  $\text{NH}_3$  — torsion. b) Optic translatory vibration

## 2. Measurements

Measurements were made on the Dubna time-of-flight spectrometer for IINS [4] installed at the pulsed reactor IBR. Fig. 3 presents the geometry used in the measurements: Neutrons produced in pulses passed the distance moderator-sample, and after the  $90^\circ$ -scattering were reflected elastically by a Zn-monocrystal, before being detected by  $\text{BF}_3$ -counters connected with a multichannel time analyser. The Bragg reflection by the

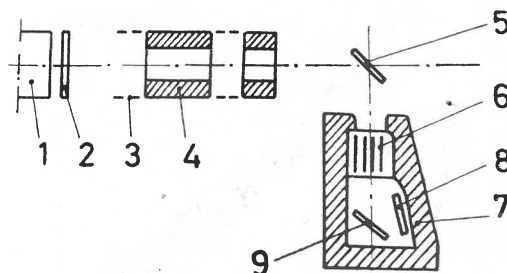


Fig. 3. Scheme of the Dubna IINS spectrometer. 1 - pulsed reactor IBR, 2 - moderator, 3 - vacuum tubes, 4 - collimators, 5 - sample, 6 - cooled Be-filter with collimating Cd-plates, 7 - shield, 8 -  $\text{BF}_3$  counters, 9 - Zn monocrystal

Zn-crystal fixed the energy  $E'$  of scattered neutrons. The incident neutron energy  $E_0$  was selected by measuring the time-of flight in a corresponding channel of the time analyser. In this way the energy transfer  $\Delta E = E_0 - E'$  could be measured similarly as in Raman scattering of light.

The parameters characterizing the spectrometer are [4]: Flight path: moderator-sample,  $L_1 = 20, 30$  m; Flight path: sample — Zn — detector,  $L_2 = 1.18$  m; Fixed energy of scattered neutrons  $E' = 5$  meV; Resolution  $\frac{\Delta\lambda}{\lambda} = \text{ca. } 3.5\%$  ( $\lambda$  is neutron wavelength). Energy of incident neutrons variable in range *ca.* 100 — *ca.* 5 meV.

Polycrystalline samples of *ca.* 1 mm thickness were placed in a cryostat, which made it possible to perform measurements at any temperature between that of liquid nitrogen and

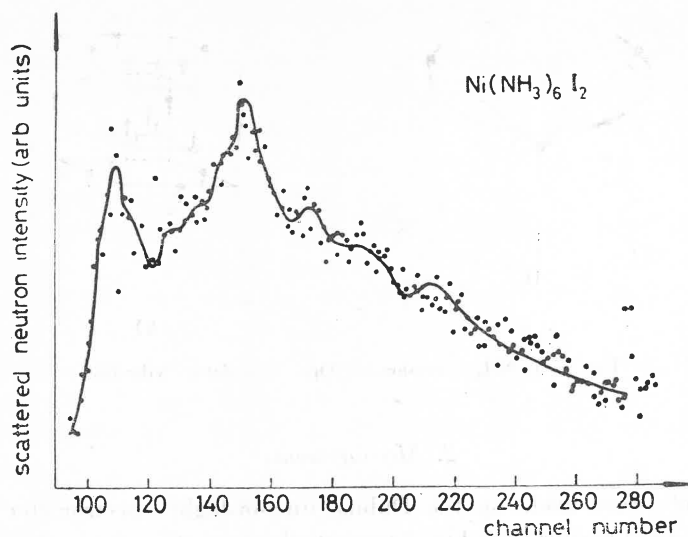


Fig. 4. Intensity of neutrons inelastically scattered from  $\text{Co}(\text{NH}_3)_6\text{I}_2$  vs. analyser channel number. Background subtracted

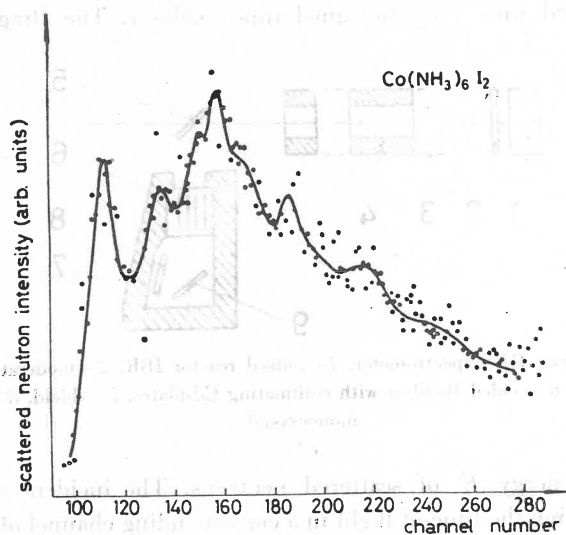


Fig. 5. Intensity of neutrons inelastically scattered from  $\text{Ni}(\text{NH}_3)_6\text{I}_2$  vs. analyser channel number. Background subtracted

room. The IINS spectra were obtained at only one temperature of the range, this being  $113^\circ\text{K}$ .

IINS spectra obtained for the two substances are presented in Figs 4 and 5. Points correspond only to inelastically scattered neutrons, the elastic peaks not being shown.

It should be noted that the resolution was in these measurements *ca.* 3 times better than in paper [3].

### 3. Discussion of results

We applied the generally accepted procedure of passing from the scattered neutron intensity plots as shown in Figs 4 and 5 to phonon density plots  $g(\omega)$ . In calculations based upon a formula given, for instance, in [5], we adopt the usual assumptions: we take the one-phonon scattering into account, we neglect the scattering from atoms other than hydrogen, which we assume scatters only incoherently, and we assume that the Debye — Waller factor is equal to 1. With these assumptions one does not obtain the true frequency distribution (or phonon density) but only an effective one. Many arguments have been put forward, however, that the difference between the true and effective  $g(\omega)$  is small for hydrogenous, polycrystalline materials. It should be noted that in view of the one-phonon approximation used, the possible two-phonon peak appears in  $g(\omega)$  as a peak at a frequency corresponding to a combination of those of component phonons. The plots obtained by us from the scattered neutron intensities for the two substances are presented in Figs 6 and 7. The  $\omega$ -values corresponding to  $g(\omega)$ -peaks are assembled in Tables I and II and compared with the data of papers [1], [2], [3].

Passing to a discussion of the results obtained, we note above all a very good agreement between our data and those from calorimetry work [1] interpreted as  $\text{NH}_3$ -torsion. It had to be expected that, as this kind of motion is mostly determined by the internal structure of the complex ion octaheder, it would not be much affected by the temperature. This motion probably also leads to the rather flat optic branches of phonon dispersion curves, thus giving well-defined maxima in  $g(\omega)$ .

We attribute the next peak to optic translatory vibration on the basis of a comparison with IR results [2]. As a matter of fact, if the interpretation is correct this peak should shift towards lower frequencies as the temperature increases, because of a sensitivity of lattice

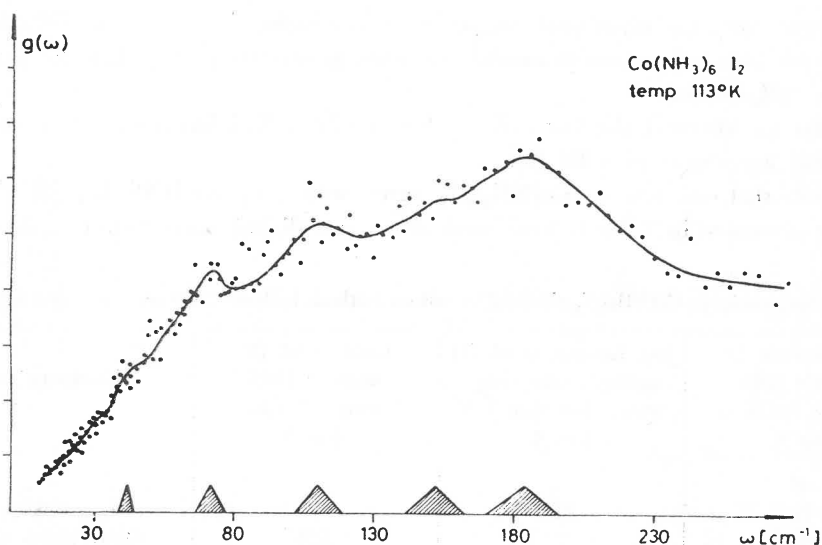


Fig. 6.  $g(\omega)$  function for  $\text{Co}(\text{NH}_3)_6\text{I}_2$ . Plot corresponds to the channel number interval 150–280 of Fig. 4, Resolution at peak positions is shown

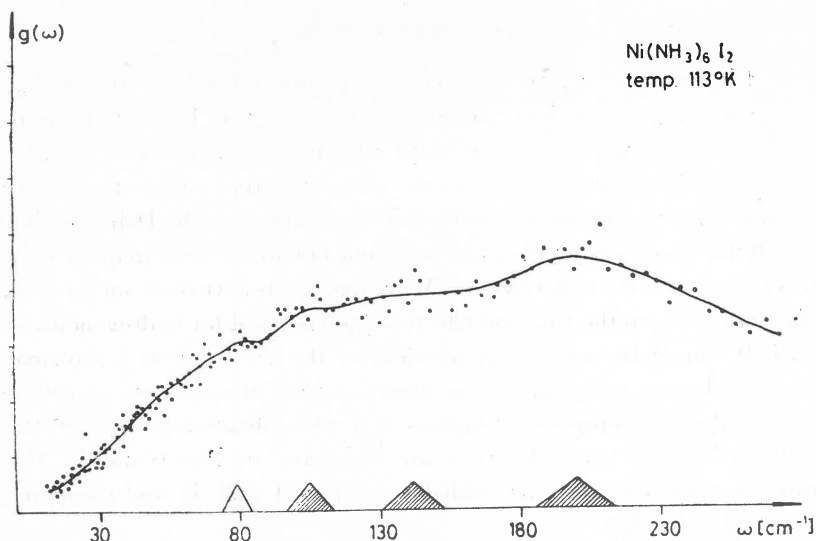


Fig. 7.  $g(\omega)$  function for  $\text{Ni}(\text{NH}_3)_6 \cdot \text{I}_2$ . Plot corresponds to the channel number interval 150–280 of Figs 5. Resolution at peak positions is shown

modes to temperature. We believe that this temperature effect is responsible for the difference between our values (105–110  $\text{cm}^{-1}$ ) and that of paper [2] (81  $\text{cm}^{-1}$ ).

Hence, we feel that the coincidence between IR and calorimetry values mentioned in § 1 is completely fortuitous. It should also be mentioned that even if we do not use the argument of inactivity of  $\text{NH}_3$ -torsion in IR we must come to the conclusion that such  $\text{NH}_3$  motion could not be visible at room temperature where the  $\text{NH}_3$  — rotation becomes quasi-free.

The next, very indistinct peak we attribute to a higher harmonics of  $\text{NH}_3$ -torsion, as it appears for both substances at nearly two times greater frequency than the peak interpreted as  $\text{NH}_3$ -torsion.

Finally, we interpret the last peak as the N—Me—N deformation vibration, on the basis of this agreement with IR [2].

We note that our data for  $\text{Co}(\text{NH}_3)_6 \cdot \text{I}_2$  agree with previous IINS data [3] which, before being presented in Table I, were recalculated and slightly corrected. The old data are,

TABLE I  
Vibrational frequencies in  $\text{Co}(\text{NH}_3)_6 \cdot \text{I}_2$  obtained by various methods (only  $\omega < 300 \text{ cm}^{-1}$  are taken into account)

This work method: IINS temp.: 113°K [ $\text{cm}^{-1}$ ]	Van Kempen <i>et al.</i> [1] method: calorimetry temp.: less than 1°K [ $\text{cm}^{-1}$ ]	Jakób <i>et al.</i> [3] method: IINS temp.: 123°K [ $\text{cm}^{-1}$ ]	Interpretation
43			
72	81	84	$\text{NH}_3$ — torsion
110		124	Optic. trans. vibr.
152			$2 \times \text{NH}_3$ — torsion
184		207	N—Co—N deform. vibr.

of course, much more smeared out owing to the resolution factor (Fig. 8). Some systematic deviations of the peak positions at higher  $\omega$ 's may be caused by insufficient accuracy in flight-path ( $L_1$  and  $L_2$ ) determination in the old measurements.

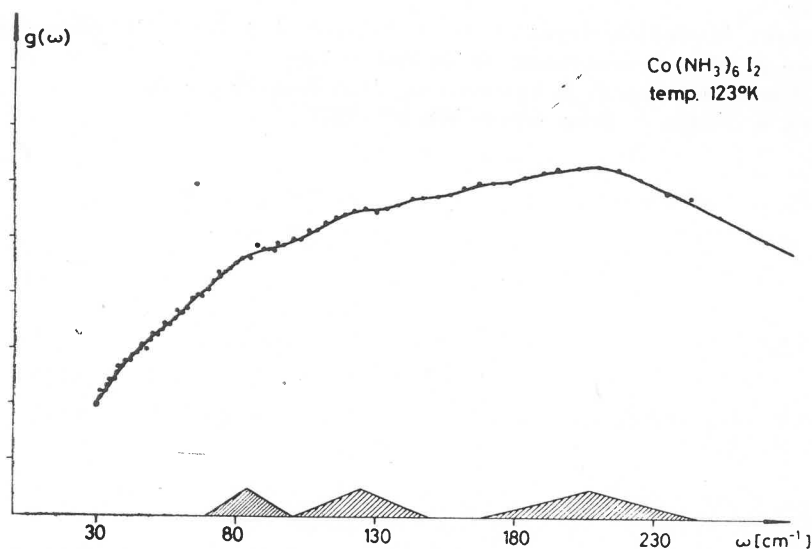


Fig. 8.  $g(\omega)$  function for  $\text{Co}(\text{NH}_3)_6\text{I}_2$  obtained on the basis of data of the paper [3]. Resolution at peak positions is shown

We believe that it will be possible in the near future to work out in our Laboratory a theoretical model describing the low frequency part of the  $g(\omega)$  function.

We would like to express our gratitude to the late Professor Henryk Niewodniczański for the help and interest he showed during the completion of this work.

TABLE II

Vibrational frequencies in  $\text{Ni}(\text{NH}_3)_6\text{I}_2$  obtained by various methods (only  $\omega < 300 \text{ cm}^{-1}$  are taken into account)

This work method: IINS temp. 11K $3^\circ$ [ $\text{cm}^{-1}$ ]	Van Kempen <i>et al.</i> [1] method: calorimetry temp.: less than 1 $^\circ$ K [ $\text{cm}^{-1}$ ]	Sacconi <i>et al.</i> [2] method: IR temp.: room [ $\text{cm}^{-1}$ ]	Interpretation
80	79		$\text{NH}_3$ — torsion
105		81	Optic transl. vibr.
142			$2 \times \text{NH}_3$ — torsion
200		216	N-Ni-N deform. vibr.

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