STUDY OF INTERNAL ROTATION OF NH_3 GROUPS IN CRYSTALLINE COMPLEX COMPOUNDS OF THE TYPE $Me(NH_3)_6I_2$ BY INFRARED SPECTROSCOPY

J. M. Janik*, J. A. Janik, A. Migdał, G. Pytasz

Institute of Chemistry of the Jagellonian University, Cracow*
Institute of Physics of the Jagellonian University, Cracow**
Institute of Nuclear Physics, Kraków

(Received March 1, 1971)

IR perpendicular vibrations of NH_3 groups were studied *versus.* temperature. From their broadening, barriers to rotation of NH_3 groups in $Co(NH_3)_6I_2$ and $Ni(NH_3)_6I_2$ were determined as being respectively: 225 cm^{-1} and 209 cm^{-1}. These results are compared with those previously obtained by calorimetry and IINS.

1. Introduction

There are two types of information concerning internal rotation of the NH_3 groups in $Co(NH_3)_6I_2$ and Ni $(NH_3)_6I_2$. Van Kempen *et al.* [1] obtained from the specific heat anomaly below 1°K rotational barriers as being respectively 254°K and 250°K (177 cm^{-1} and 175 cm^{-1}). Torsional frequencies calculated from these barriers are 116°K and 114°K (81 cm^{-1} and 79 cm^{-1}) respectively. Jakób *et al.* [2] obtained for $Co(NH_3)_6I_2$ from incoherent inelastic neutron scattering (IINS) a vibration at 84 cm^{-1} and later on Janik *et al.* [3], continuing the IINS measurements, obtained for $Co(NH_3)_6I_2$ and $Ni(NH_3)_6I_2$ evidence of vibrations at frequencies amounting respectively to 72 cm^{-1} and 80 cm^{-1}. In this way the IINS measurements supported barrier values as suggested in [1].

Recently a new method has been applied for the determination of rotational barriers in liquids and crystals. This method uses the temperature dependence of the profile of internal vibration lines of the molecular group performing rotation [4], [5], [6], [7], [8]. In particular Leech *et al.* [7], [8] have applied this technique to the crystalline complex compounds $Pd(NH_3)_2I_2$, $Pd(NH_3)_2Cl_2$ and $Au_2(CH_3)_4J_2$ and have obtained, for NH_3 or CH_3 rotational barriers, the values 210 cm^{-1}, 430 cm^{-1}, and *ca* 300 cm^{-1}.

** Address: Instytut Fizyki, Uniwersytet Jagielloński, Kraków 16, Reymonta 4, Poland.

This work is an attempt at a similar adaptation of the IR technique to the complexes $Co(NH_3)_6I_2$ and $Ni(NH_3)_6I_2$, in order to compare the results with those previously obtained by IINS and calorimetry.

2. *Experimental method*

IR absorption measurements were performed on the UR-10 Zeiss spectrometer at the Institute of Chemistry of the Jagellonian University in Cracow. They covered the wave number range 400 cm^{-1}—3800 cm^{-1}. Samples, in the form of $KBr+Co(NH_3)_6I_2$ (or $Ni(NH_3)_6I_2$) pellets, were situated in a vacuum cryostat with KBr windows. Measurements were made in relation to a pure KBr pellet (situated in the second beam).

The cryostat enabled us to perform measurements at any temperature between that of liquid nitrogen and room temperature.

During the measurements it was discovered that the temperature on the edge of the sample differs from that of its central part. In order to see how great these differences are we measured the temperatures at the edge and in the central part of the sample simultaneously several times. In this way we could deduce the real temperature of the sample in three series of measurements with $Co(NH_3)_6I_2$ and in two series with $Ni(NH_3)_6I_2$, for which temperature measurements were done at the edge only. In addition to this we performed one additional series of measurements for each substance in which the temperature was measured directly near the central part of the sample. As it may be seen from the results the agreement between all the series is good.

3. *Results and discussion*

IR absorption measurements were made in the temperature range 135°K–301°K. As it was mentioned they were performed four times for $Co(NH_3)_6I_2$. The measurements for $Ni(NH_3)_6I_2$ were performed three times. Fig. 1 presents exemplarily chosen results of the first series of $Co(NH_3)_6I_2$; asterisks (*) denote peaks whose profile was studied in dependence on temperature, *i.e.*: the peak at *ca* 640 cm^{-1} corresponding to δ-rocking NH_3 and the peak at *ca* 1600 cm^{-1} corresponding to δ-asym. NH_3; these are so-called perpendicular vibrations in which one should expect the temperature dependence caused by NH_3-rotation. The triangle (Δ) denotes the peak at 1200 cm^{-1} (parallel vibration) whose profile should not depend on temperature; this lack of temperature dependence was indeed observed.

An important methodical problem in the profile investigation lies in the isolation of the peak under consideration, *i.e.*: in subtraction of the background on which the peak is superimposed. In this work we accept for background a hand drawn curve. This background was subtracted from the measured absorption.

In principle there exist two methods which apply the peak profile to a determination of the rotational barriers. One method, suggested by Bulanin and Orlova [5], takes the so-called rotational wings which appear at both sides of the vibrational peaks into account. One accepts that the intensity of the central part is caused by non-rotating molecules, whereas the wing intensity is connected with molecules whose rotational quantum numbers correspond to energy levels above the top of the barrier. Thus the intensity ratio I_{wings}/I_{total}

gives the barrier height. The second method, suggested by Rakov [6], may be applied if no distinct rotational wings appear but only a broadening of the absorption peak with temperature. Rakov distinguishes three mechanisms of the broadening as connected with a) dissipation of the oscillatory quantum energy into thermal energy (γ_1) b) interaction of the vibrating molecule with its neighbours (γ_2), and c) rotational reorientation of the molecule through jumps over the rotational barrier (γ_3). From these three mechanisms only the third one depends on temperature, as given by the formula:

$$\gamma_3 = \text{const}\, e^{\frac{-U_{act}}{kT}}$$

Thus, if one measures ln γ_3 *versus* $1/T$, one should obtain a straight line, whose slope should give U_{act}.

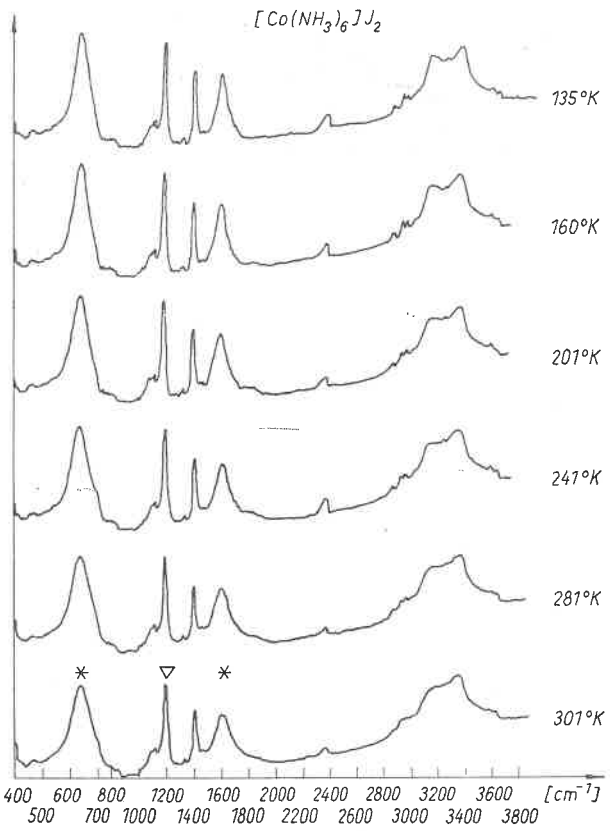
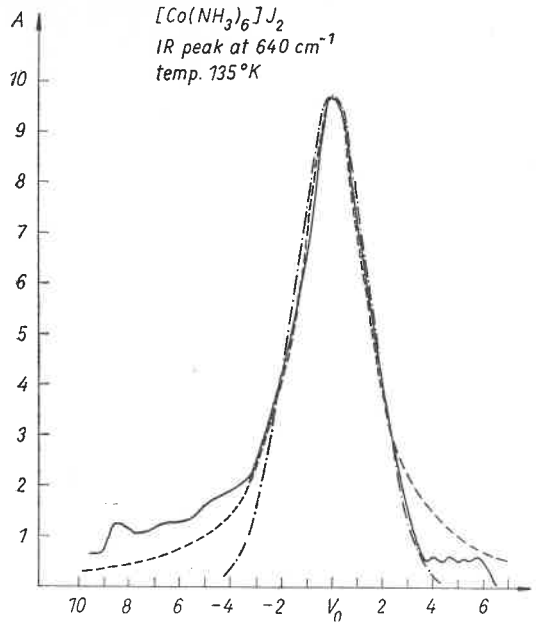
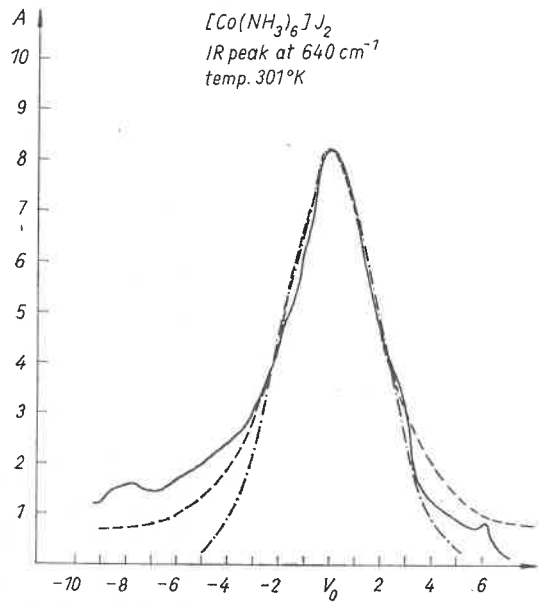


Fig. 1. IR absorption spectra for $Co(NH_3)_6I_2$ at various temperatures. Asterisks (*) indicate the temperature dependent peaks. Triangle ($\triangle$) indicates the temperature independent peak.

As peaks observed by us (*in Fig. 1) did not show distinct rotational wings, we decided to apply the Rakov method. In connection with this we had another (besides the background subtraction procedure) methodical difficulty which lay in the problem of subtraction of


[Co(NH3)6]J2
IR peak at 640 cm-1
temp. 135°K
A
10
9
8
7
6
5
4
3
2
1
10
8
6
-4
-2
V0
2
4
6

a


[Co(NH3)6]J2
IR peak at 640 cm-1
temp. 301°K
A
10
9
8
7
6
5
4
3
2
1
-10
-8
-6
-4
-2
V0
2
4
6

b

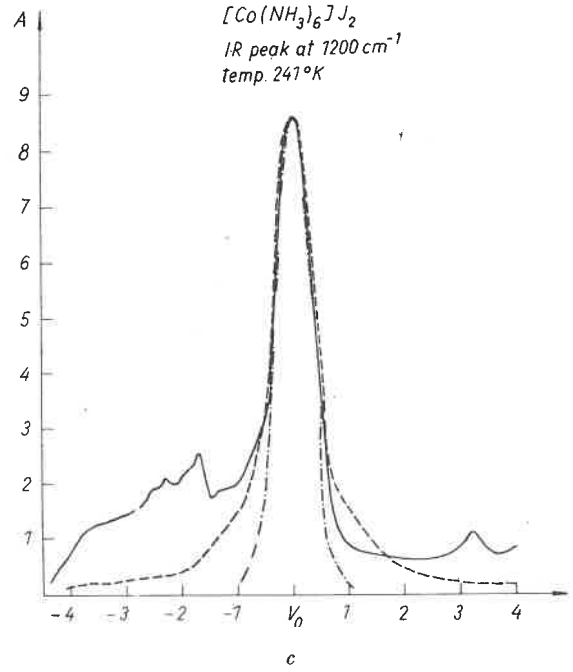
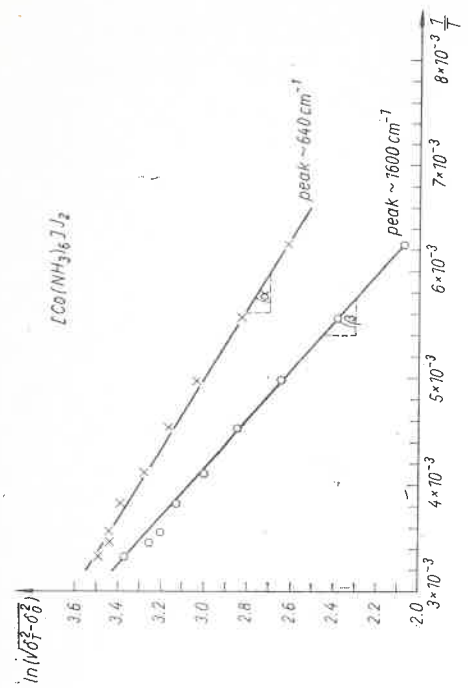


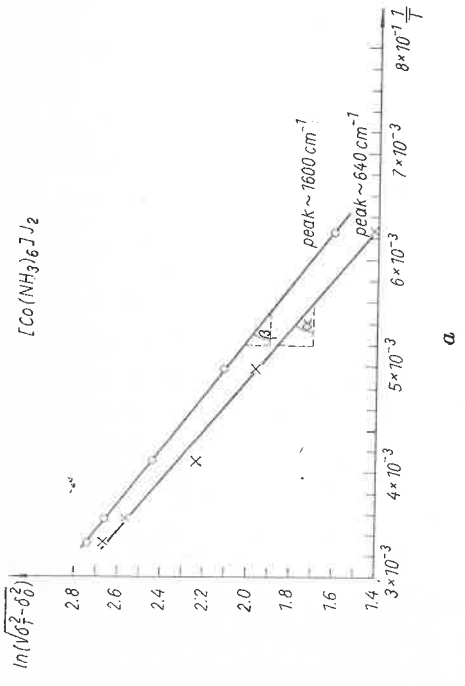
Fig. 2. Gaussian (·— ·— ·—) and Lorentzian fits of the measured (———) peaks. *a* — for 640 cm^{-1} peak, temperature 135°K; *b* — for 640 cm^{-1} peak, temperature 301°K; *c* — for 1200 cm^{-1} peak, temperature 241°K

the temperature independent component from the measured widths. Rakov accepts the Lorentzian character of the three processes (a), (b), (c) and hence he subtracts from the measured full width at the half maximum (δ_T) the width (δ_0) measured at the lowest temperatures, where reorientational jumps no longer play any role. However, the assumption of the Lorentzian character of the profile is to a certain point arbitrary, and there is some experimental material indicating that the true profile lies between a Gaussian and Lorentzian curve (see, for instance, [9]).

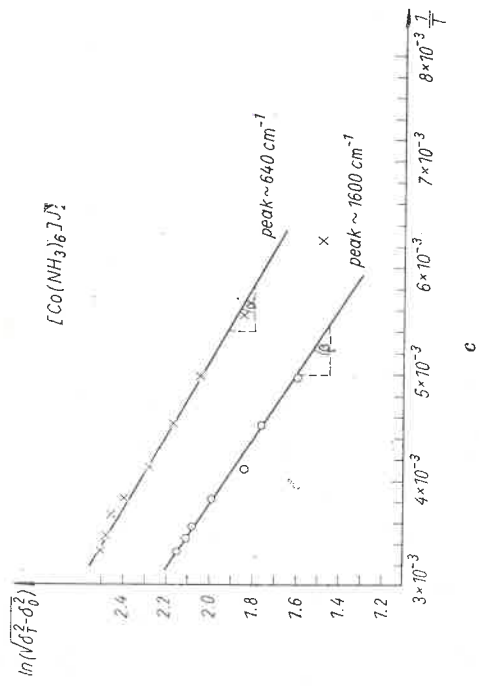
Comparison of the Lorentzian and Gaussian fits made by us gives for a temperature dependent peak at *ca* 640 cm^{-1} the results presented in Fig. 2*a* and *b*, and for a temperature independent peak 1200 cm^{-1} the result presented in Fig. 2*c*. We admit, that from this comparison we cannot establish unequivocably the superiority of the Gaussian approximation to the Lorentzian one. However, we feel that the background subtraction is more properly taken in consideration at the right side than at the left side of the peaks, because of the unfavourable existence at the left side of some extra maxima. We therefore consider that the comparison of the experimental curve with Gaussian and Lorentzian fits is more valuable at the right side of the peaks and hence it favourises rather the Gaussian fit. If we accept this, we must not directly subtract from the full width the temperature independent width component, but we shall take the square root from the differences of squares of two widths $(\sqrt{\delta_T^2 - \delta_0^2})$.

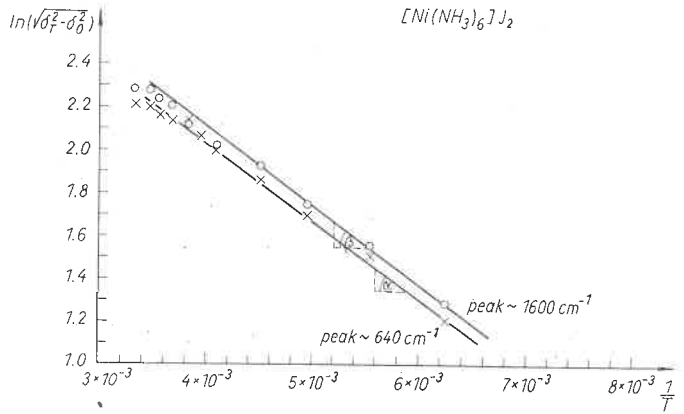
The thus processed data are presented in Fig. 3*a*, *b*, *c*, *d*, *e* in the form of the dependence


[Co(NH3)6]J2
peak ~ 1600 cm-1
peak ~ 640 cm-1
a

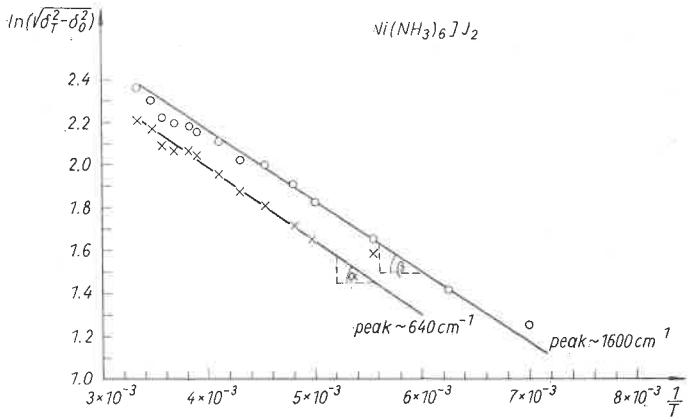

[Co(NH3)6]J2
peak ~ 1600 cm-1
peak ~ 640 cm-1
b

[Co(NH3)6]J2
peak ~ 1600 cm-1
peak ~ 640 cm-1
c

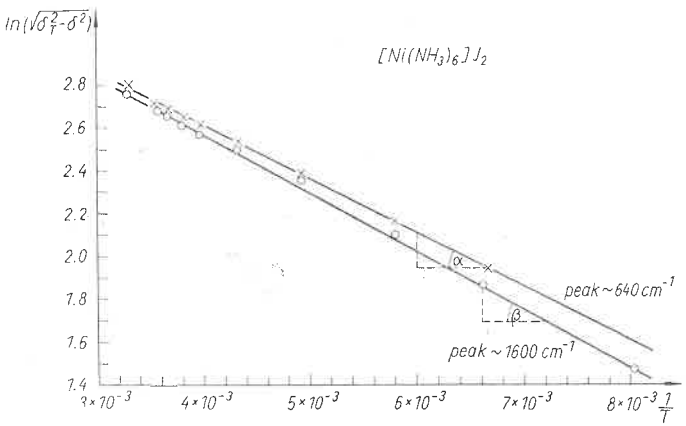

[Co(NH3)6]J2
peak ~ 1600 cm-1
peak ~ 640 cm-1
d



e



f



g

Fig. 3. Logarithm of the reorientational broadening *versus* $1/T$. *a* — $Co(NH_3)_6I_2$ first run, *b* — $Co(NH_3)_6I_2$ second run, *c* — $Co(NH_3)_6I_2$ third run, *d* — $Co(NH_3)_6I_2$ fourth run, *e* — $Ni(NH_3)_6I_2$ first run, *f* — $Ni(NH_3)_6I_2$ second run, *g* — $Ni(NH_3)_6I_2$ third run

of logarithm of the reorientational broadening *versus* $1/T$. We may observe that the dependences lie well on straight lines from whose slopes we are able to determine the rotational barrier U_{act}. Results are assembled in Tables I and II.

TABLE I

Rotational barrier U_{act} for $Co(NH_3)_6I_2$ from measurements of the broadening of bands δ_{rock} and δ_{asym} of NH_3 groups *versus* temperature

First series	
from band $\delta_{rock}(\sim 640\ cm^{-1})$	$U_{act} = 277\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 259\ cm^{-1}$
Second series	
from band $\delta_{rock}(\sim 640\ cm^{-1})$	$U_{act} = 197\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 207\ cm^{-1}$
Third series	
from band $\delta_{rock}(\sim 640\ cm^{-1}$	$U_{act} = 197\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 287\ cm^{-1}$
Fourth series	
from band $\delta_{rock}(\sim 640\ cm^{-1})$	$U_{act} = 197\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 180\ cm^{-1}$
	average $U_{act} = 225\ cm^{-1}$

TABLE II

Rotational barrier U_{act} for $(Ni(NH_3)_6I_2$ from measurements of the broadening of bands δ_{rock} and δ_{asym} of NH_3 groups *versus* temperature

First series	
from band $\delta_{rock}(\sim 640\ cm^{-1})$	$U_{act} = 228\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 214\ cm^{-1}$
Second series	
from band $\delta_{rock}(\sim 640\ cm^{-1})$	$U_{act} = 228\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 225\ cm^{-1}$
Third series	
from band $\delta_{rock}(\sim 640\ cm^{-1})$	$U_{act} = 173\ cm^{-1}$
from band $\delta_{asym}(\sim 1600\ cm^{-1})$	$U_{act} = 184\ cm^{-1}$
	average $U_{act} = 209\ cm^{-1}$

TABLE III

A comparison of rotational barriers for NH_3 groups in $Co(NH_3)_6I_2$ and $Ni(NH_3)_6I_2$ obtained by various methods

$Co(NH_3)_6I_2$

Van Kempen *et al.* [1] calorimetry	Jakób *et al.* [2] IINS	Janik *et al.* [3] IINS	this work IR
177 cm^{-1}	184 cm^{-1}	156 cm^{-1}	225 cm^{-1}

$Ni(NH_3)_6I_2$

Van Kempen *et al.* [1] calorimetry	Janik *et al.* [3] IINS	this work IR
175 cm^{-1}	177 cm^{-1}	209 cm^{-1}

A comparison of these results with those obtained by the IINS and calorimetric methods is presented in Table III.

The agreement between results obtained by various methods is good. We should not, however, overestimate this agreement because in each of the described methods one makes some more or less arbitrary assumptions. Thus results should be treated as giving only the barrier height estimate, which may differ from the true height even by 100%.

We should, for instance, note that an acceptance of the Lorentzian instead of the Gaussian peak form would lead to another procedure of subtraction of the temperature independent component, which would give for $Co(NH_3)_6I_2$ an average barrier of *ca* 400 cm^{-1} instead of 225 cm^{-1}.

Our thanks are due to Messrs T. Sarga and W. Olejarczyk for technical help.

REFERENCES

[1] H. Van Kempen, T. Garafano, A. R. Miedema, W. J. Huiskamp, *Physica*, **31**, 1096 (1965).
[2] W. Jakób, J. M. Janik, J. A. Janik, A. Bajorek, K. Parliński, M. Sudnik-Hrynkiewicz, *Physica*, **35**, 441 (1967).
[3] J. A. Janik, W. Jakób, J. M. Janik, *Acta Phys. Polon.*, **A38**, 467 (1970).
[4] M. O. Bulanin, H. D. Orlova, *Optika i Spektrosk.*, **4**, 569 (1958).
[5] M. O. Bulanin, H. D. Orlova, *Optika i Spetrosk.*, **15**, 208 (1963).
[6] A. W. Rakov, *Trudy Fiz. Instituta im. Lebiedieva*, **27**, 111 (1964).
[7] R. C. Leech, D. B. Powell, N. Sheppard, *Spectrochim. Acta*, **21**, 559 (1965).
[8] R. C. Leech, D. B. Powell, N. Sheppard, *Spectrochim. Acta*, **22**, 1931 (1966).
[9] J. P. Hawranek, *Wiadomości Chemiczne* (in Polish), **24**, 225 (1970).