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Frequencies and Temperature-Effects in the Vibrational Spectra of the Metal-Hydrate Complexes in $NiSnCl_6 \cdot 6\,aqu$ and in $NiSO_4 \cdot 6\,aqu$ *

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We have investigated the internal vibrations of metal hydrate complexes in ionic single crystals and their interactions with the phonon system of the lattice, by observing the Raman spectra and infrared reflection spectra with polarized light at different temperatures T ($2\,K \leqq T \leqq 300\,K$). As special systems the octahedral nickel hydrate complexes in $NiSnCl_6 \cdot 6\,H_2O$, $NiSnCl_6 \cdot 6\,D_2O$ and in $NiSO_4 \cdot 6\,H_2O$, $NiSO_4 \cdot 6\,D_2O$ have been chosen. For $NiSnCl_6 \cdot 6\,aqu$ a complete interpretation of the spectra is given, starting from the assumption of isolated metal hydrate complexes and $SnCl_6^{--}$-ions as structural units. The discussion of the spectra of the sulfate crystal is based on the corresponding assumption. However, here an unambiguous assignment of all lines observed was not possible.

The most prominent feature of all spectra is the strong temperature dependence of the line widths which is much more pronounced than in anhydrous crystals in the same temperature interval. This effect is qualitatively explained in terms of the anharmonicity of the potential by which the water molecules are bound in the crystal lattice. Simple models for this potential are discussed.

Introduction

The problem of assigning infrared or Raman lines to certain lattice vibrations of the water molecules in hydrated ionic crystals in terms of translational and (or) librational modes has been discussed in several papers (e. g. [1, 2]). The central question is whether the hydrate complexes consisting of water molecules surrounding a central metal ion can be regarded as quasi-molecules in the sense of lattice dynamics, as they are regarded as structural units of the crystalline lattice. Additional interest in these problems arose since it was shown that the electronic excitation energy of rare earth and transition metal ions in hydrated crystals can be transferred to the lattice via the vibrational excitation of the shell of water molecules [3]. The relaxation times of the excited electronic states are thus determined in part by the density of the vibrational states of this surrounding shell. The efforts towards an observation and unambiguous assignment of all the transitions predicted by group theory for a hydrate complex of given symmetry have, however, not been completely successful even in cases where IR as well as Raman measurements were available, probably because these measurements had been performed at room temperature. Below about 800 cm^{-1} the room temperature spectra of hydrates are considerably broadened compared to the low temperature spectra. The effects are similar to those recently observed in the IR spectrum of beryll [4] at much higher temperatures and in the IR spectra of molten alkali nitrates and sodium nitrate [5]. Therefore a proper assignment of the observed lines to the expected lattice vibrations can be more easily achieved if the analysis is based on the low temperature spectra. Recently Lafont et al. have reported more complete measurements on this subject [2]. Spectra recorded in the intermediate tempera-

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ture range between room temperature and liquid helium temperature can support the assignment if the different temperature dependence of modes of different origin are taken into account. Moreover the temperature dependence of the spectra is the starting point for a discussion of the degree of anharmonicity of the lattice potential involved.

Here we present the IR reflection spectra at near-normal incidence at $T = 300$ K, 200 K, 80 K, and 15 K and the Raman spectra at $T = 300$ K and $T = 2$ K of oriented single crystals of $NiSnCl_6 \cdot 6\,H_2O$ and α-$NiSO_4 \cdot 6\,H_2O$ obtained in polarized light as well as the spectra of the deuterated compounds.

The isotope effect on deuteration helps to distinguish the internal vibrations of the hydrate complex from the external lattice vibrations and from iternal vibrations of the molecular anions.

Experimental

For the measurement of the IR reflection spectra we used above 300 cm^{-1} a Leitz prism spectrometer [6] and between 80 and 400 cm^{-1} a Grubb-Par sons-Fourier spectrometer [7]. From the measured reflectivity we calculated the imaginary part of the complex dielectric constant ε'' as a function of wavenumber by a Kramers-Kronig transformation. The prism instrument was used in a single beam mode of operation with digital data processing. The Fourier spectrometer was equipped with a germanium bolometer operating at liquid helium temperature. As temperature baths for the cold-finger cryostat we used solid CO_2 in acetone, liquid nitrogen and liquid helium to reach surface temperatures of the polished specimens near 300 K, 200 K, 80 K and 15 K. The low-temperature Raman experiments were performed by immersing the crystal in superfluid helium. The specimens were cut from single crystals of walnut-size obtained by isothermal evaporation of the saturated solutions at temperatures near 50 °C. The spectra were excited by an Argon ion laser ($\lambda =$ 4880 Å). The instrumental set up is described in [8]. The scattering tensors for $NiSnCl_6 \cdot 6$ aqu (symmetry C_{3i}) are [9]:

$$A_g: \begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}; \quad E_g: \begin{pmatrix} c & d & e \\ d & -c & f \\ e & f & \end{pmatrix}; \quad E_g: \begin{pmatrix} d & -c & -f \\ -c & -d & e \\ -f & e & \end{pmatrix}.$$

The lattice vibrations of both symmetry types can be observed independently. The emission line $\lambda =$ 4880 Å of the Argon ion laser is well suited for the excitation of the spectra, because the absorption coefficient of the crystal is sufficiently small at this wavelength, so that the laser can be run with maximum power without damaging the crystal.

The scattering tensors for the Symmetry D_4 of α-$NiSO_4 \cdot 6$ aqu are [9]:

$$A_1: \begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}; \quad B_1: \begin{pmatrix} c & & \\ & -c & \\ & & \end{pmatrix}; \quad B_2: \begin{pmatrix} & d & \\ d & & \\ & & \end{pmatrix};$$

$$E(-y): \begin{pmatrix} & & e \\ & & \\ e & & \end{pmatrix}; \quad E(x): \begin{pmatrix} & & \\ & & e \\ & e & \end{pmatrix}.$$

A rotation of the crystal by 45° around the z axis ($x \to x'$, $y \to y'$) leaves the A_1-tensor unchanged. For the other tensors one obtaines

$$B_1: \begin{pmatrix} & c & \\ c & & \\ & & \end{pmatrix}; \quad B_2: \begin{pmatrix} -d & & \\ & d & \\ & & \end{pmatrix};$$

$$E(-y'): \frac{1}{\sqrt{2}} \begin{pmatrix} & & -e \\ & & e \\ -e & e & \end{pmatrix}; \quad E(x'): \frac{1}{\sqrt{2}} \begin{pmatrix} & & e \\ & & e \\ e & e & \end{pmatrix}.$$

The transverse lattice vibrations of type E were recorded using the scattering geometry $y\,(y\,z)\,z$. The geometry $y'\,(z\,y')\,z$ leads to identical results. The B-spectra were obtained in the geometry $y\,(x\,y)\,z$ using a specimen of cylindrical symmetry around the optical axis (z-axis). If the orientation of the crystal and the polarizers are chosen to give the B_1-spectrum, one only has to rotate the crystal around its z-axis by 45° to observe the B_2-spectrum which could be done in superfluid helium as well as at room temperature.

α-$NiSO_4 \cdot 6$ aqu shows optical activity. Room temperature measurements of transmission and optical activity [10] show that the transmissivity has a maximum near 4900 Å and that the rotatory power vanishes at this wavelength. Therefore the emission line at $\lambda = 4880$ Å of the Argon ion laser is suitable for this crystal too, if the laser power is reduced appropriately. At $\lambda = 4880$ Å and $T = 300$ K the rotatory power is 0.2°/mm but increases with decreasing temperature [11]. At 2 K it reaches the value 1°/mm [all numerical values for light travelling along the optical (z-) axis]. The gyration tensor is of the form $g_{ij} \cdot \delta_{ij}$ [12]. The elements $g_{xx} = g_{yy}$ are unknown. The measurements were not seriously affected by the depolarising effect of the optical activity as the observed spectra generally show clear polarization properties. Difficulties only occured in the B_1- and B_2-spectra which seemed not to be completely separated from one another. A possible explanation for this effect can be seen in the pronounced layer structure of the crystal. Twinning effects with respect to a twisting of these layers against one another could be present without being detectable with a polarizing microscope.

Crystal Structure

a) $NiSnCl_6 \cdot 6\,aqu$

The crystal structure of $NiSnCl_6 \cdot 6\,H_2O$ (C_{3i}^2) can be described by a CsCl lattice with a rhombohedral distortion, composed of $[Ni(OH_2)_6]^{2+}$ and $SnCl_6^{2-}$ ions of nearly equal size. The elementary cell contains one formular unit. The Ni – O-distances within the hydrate complexes are 2.4 Å. The O – Cl-distances are 3.25 and 3.35 Å [13]. The exact positions of the protons are unknown.

b) α-$NiSO_4 \cdot 6\,aqu$

There are two enantiomorphous forms of this crystal of space groups D_4^4 and D_4^8 [13]. The elementary cell contains four formular units. The structure can be thought of as being composed of $Ni(OH_2)_6^{2+} - SO_4^{2-}$ dumb-bells, located on somewhat distorted screw-lines along the z axis in such a way, that the dumb-bells are transformed into one another by a rotation of 45 degrees and a translation of $\frac{1}{4}\,c_0$. The dumb-bell to start with lies in the ground plane ($z = 0$) of the unit cell along one diagonal. The site symmetry of the hydrate complexes and that of the sulfate ions is C_2, the water molecules have the site symetry C_1. The $Ni - OH_2$ distances are 2.02 and 2.04 Å. Contact between the hydrate complexes and the SO_4-groups is made along $O - H_2O$ distances $\geqq 2.69$ Å. The crystal possesses a layer structure perpendicular to the z axis so that the xy plane is a plane of perfect cleavage. In this plane two different types of twofold axes occur, one pair along the a-axes of the unit cell and one along the (110)- and ($\bar{1}$10)-directions respectively. The group theoretical analysis must be based on one of these systems of axes being chosen as the xy-system.

Group Theoretical Analysis of the Lattice Vibrations

The free $SnCl_6$ ion (symmetry O_h) has normal vibrations of types A_{1g}, E_g, $2\,F_{1u}$, F_{2g}, and F_{2u}. The free SO_4^{--}-ion (symmetry T_d) has normal vibrations of types A_1, E, and $2\,F_2$ [14]. A "free" octahedral metal hydrate complex is of symmetry T_h and has normal vibrations of types $3A_g$, A_u, $3E_g$, E_u, $5F_g$ and $8F_u$ [15].

a) $NiSnCl_6 \cdot 6\,aqu$

The following correlations exist between O_h, T_h and C_{3i}:

free ion	crystal	free ion	crystal
A_{1g}, A_g	A_g	A_u	A_u
E_g	E_g	E_u	E_u
F_{2g}, F_g	$A_g + E_g$	F_{1u}, F_{2u}, F_u	$A_u + E_u$
Raman active		IR active	

Table 1. Symmetry types of the lattice vibrations of $NiSnCl_6 \cdot 6$ aqu (1 a) and of $NiSO_4 \cdot 6$ aqu (1 b).

Abbreviations:

str: stretching vibration.
def: deformation vibr.
sciss: H_2O bending vibr.
twist: rotatory vibr. of the water molecules around their C_2 axes.
rock: rotatory vibr. of the water molecules around the axis of intertia $\perp C_2$, $\perp$ plane of the molecule.
wag: rotatory vibr. of the water molecules around the axis of inertia $\perp C_2$, in the plane of the molecule.
MO: metal-oxygen.

Table 1 a

		A_g	E_g	A_u	E_u	$\sum \nu_i$
acoustical vibrations	T			1	1	
external translations	T'			1	1	
external rotations	R'	2	2			
		2	2	2	2	$12 = 2 \cdot 6$
$SnCl_6^{2-}$						
ν_1; A_g		1				
ν_2; E_g			1			
ν_3; ν_4; $2F_{1u}$				2	2	
ν_5; F_{2g}		1	1			
ν_6; F_{2u}				1	1	
		2	2	3	3	$15 = 7 \cdot 3 - 6$
$Ni^{2+}(OH_2)_6$						
MO str; A_g		1				
MO str; E_g			1			
MO str; F_u				1	1	
OMO def; $F_g + 2F_u$		1	1	2	2	
OH_2 twist; A_u				1		
OH_2 twist; E_u					1	
OH_2 twist; F_g		1	1			
OH_2 rock; $F_g + F_u$		1	1	1	1	
OH_2 wag; $F_g + F_u$		1	1	1	1	
		5	5	6	6	$33 = 6 \cdot 6 + 3 \cdot 1 - 6$
H_2O						
OH str; A_g		1				
OH str; E_g			1			
OH str; $F_g + 2F_u$		1	1	2	2	
OH_2 sciss; A_g		1				
OH_2 sciss; E_g			1			
OH_2 sciss; F_u				1	1	
		3	3	3	3	$18 = 6(3 \cdot 3 - 6)$
						$78 = 3 \cdot 26$

Table 1 b

		A_1	A_2	B_1	B_2	E	$\sum \nu_i$
acoustical vibrations	T		1			1	3
external translations	T'	1	4	3	3	5	$21=3\cdot8-3$
external rotations	R'	1	5	3	3	6	$24=3\cdot8$
SO_4^{2-}							
ν_1; 981 cm^{-1}; A_1		1			1	1	
ν_2; 451 cm^{-1}; E		2			2	2	
ν_3; 1104 cm^{-1}; F_2		1	2	2	1	3	
ν_4; 613 cm^{-1}; F_2		1	2	2	1	3	
		5	4	4	5	9	$36=4$ $(3\cdot5-6)$
$Ni^{2+}(OH_2)_6$							
MO str; A_g		1			1	1	
MO str; E_g		2			2	2	
MO str; F_u		1	2	2	1	3	
OMO def; F_g+2F_u		3	6	6	3	9	
OH_2 twist; A_u		1			1	1	
OH_2 twist; E_u		2			2	2	
OH_2 twist; F_g		1	2	2	1	3	
OH_2 rock; F_g+F_u		2	4	4	2	6	
OH_2 wag; F_g+F_u		2	4	4	2	6	
		15	18	18	15	33	$132=4$ $(6\cdot6+3\cdot1-6)$
H_2O							
OH str; A_g		1			1	1	
OH str; E_g		2			2	2	
OH str; F_g+2F_u		3	6	6	3	9	
OH_2 sciss; A_g		1			1	1	
OH_2 sciss; E_g		2			2	2	
OH_2 sciss; F_u		1	2	2	1	3	
		10	8	8	10	18	$72=4\cdot6$ $(3\cdot3-6)$
							$288=3\cdot96$

Starting from the known normal vibrations of the $SnCl_6$-ion [16] and of the metal hydrate complex [15] one obtains the results compiled in Table 1 a. The external lattice vibrations were classified according to [17].

b) a-$NiSO_4\cdot6\,aqu$

Here the following correlations exist

free ion (T_d, T_h)	**site symmetry** (C_2)	**factor group symmetry** (D_4)
A_1, A_g, A_u	A	A_1+B_2+E
E, E_g, E_u	2 A	$2\,A_1+2\,B_2+2\,E$
F_2, F_g, F_u	A+2 B	$A_1+2\,A_2+2\,B_1+B_2+3\,E$
IR active: A_2, E		Raman active: A_1, B_1, B_2, E.

Using the same procedure as above, the results obtained are given in Table 1 b.

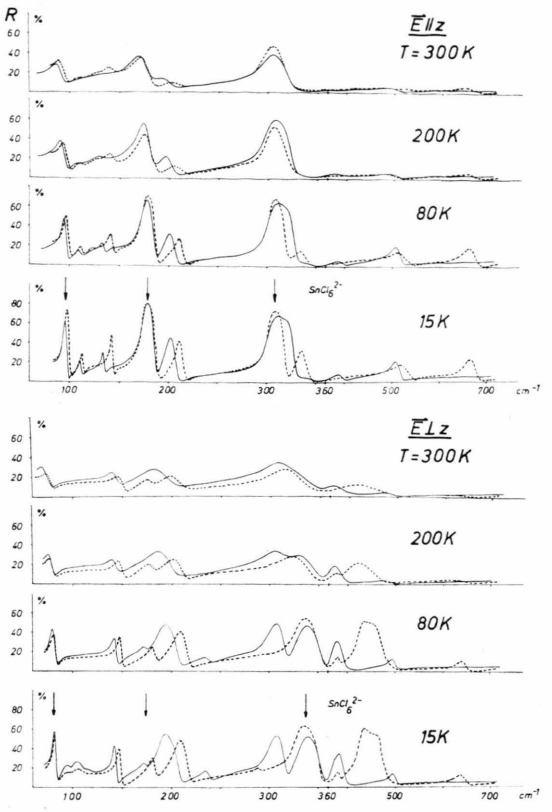

Fig. 1. IR reflection spectra of $NiSnCl_6\cdot6\,H_2O$ (broken line) and $NiSnCl_6\cdot6\,D_2O$ (solid line) with electrical vector E parallel (A_u) and perpendicular (E_u) to the optical (z)-axis. The arrows indicate transitions of the $SnCl_6^{2-}$ octahedron. Note the change in scale of the wavenumber axis at 360 cm^{-1}.

Results

a) $NiSnCl_6\cdot6\,aqu$

The IR and Raman spectra of $NiSnCl_6\cdot6$ aqu recorded in the region below 700 cm^{-1} are shown in Figures 1 to 3. Figure 4 shows the assignments of the bands observed in the IR and Raman spectra. The wavenumbers of the IR bands and their linewidths can be taken from Table 2 which contains the results of the Kramers-Kronig-transformation of the spectra. Table 3 shows the wavenumbers and the halfwidths of the Raman lines.

The bands to be asigned to internal vibrations of the $SnCl_6$-ion have been identified using the results of Debeau and Poulet [16] on hexahalogen metallates.

The predominantly rotatory internal (librational) vibrations of the metal hydrate complexes are classified according to the axis of inertia around which the

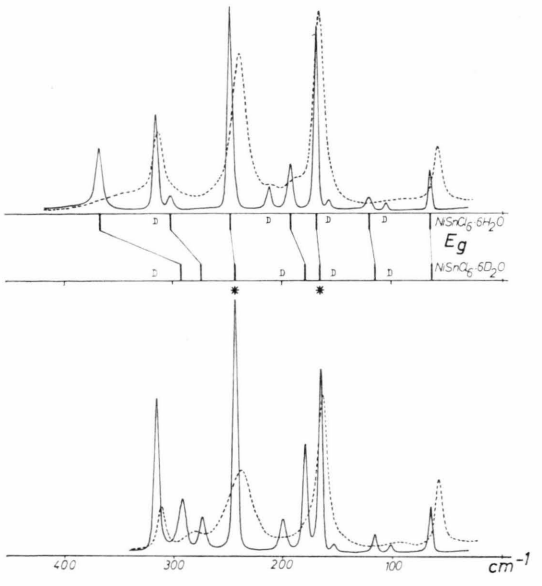

Fig. 3. Raman spectra of type E_g of $NiSnCl_6 \cdot 6\,H_2O$ and $NiSnCl_6 \cdot 6\,D_2O$. Same notations as in Figure 2.

motion of the water molecules takes place (wagging, rocking, and twisting modes, see legend of Table 1). In the spectra of the deuterated crystal the corresponding lines should be shifted according to the square root of the ratio of the moments of inertia involved. It cannot be expected however that this calculated wavenumber shift is observed strictly in all cases because admixtures of translatory symmetry coordinates to the predominantly rotatory coordinates of the same symmetry are likely to occur. Moreover in the case of nonlinear hydrogen bonds the contribution of these bonds to the force constant of the vibration is different for rocking modes on the one hand and wagging and twisting modes on the other hand. Therefore it is sometimes difficult to distinguish between rocking and wagging modes in the spectra.

(In sulfate crystals this problem is even more complicated by interactions between the rotatory internal modes of the hydrate complexes and the internal modes of the SO_4^{--}-ions. Deuteration changes this interaction because the librational water modes are shifted in energy by large amounts whereas the SO_4^{--}-modes are not. Clearly this interaction also affects the band intensities.)

Another hint for the asignment of certain bands to predominantly rotatory internal modes of the hydrate complex is given by the temperature dependence of the linewidths. It is observed that in most cases the widths of these bands demonstrate the strongest dependence on temperature in the whole spectrum with the result that some bands which are prominent at low temperatures are barely visible at 300 K.

Some of the individual assignments made will be illustrated by the following remarks; for a more detailed discussion we refer to [18].

The two A_u bands in the low temperature spectrum of the ordinary hydrate at 660 and 516 wavenumbers can be assigned to the wagging and rocking modes of type F_u in the "free" hydrate complex without any doubt. In the spectrum of the deuterated crystal these lines are found at 506 and 369 wavenumbers, i. e. they are shifted by factors $1/\sqrt{1.7}$ and $1/\sqrt{2}$. The band at 738 cm^{-1} (493 cm^{-1} in the spectrum of the deuterated crystal; line shift factor $1/\sqrt{1.68}$) arises obviously from the E_u component of the wagging mode. The E_u component of the rocking mode cannot be easily identified. In the spectrum of the ordinary hydrate the intensive band at 426 cm^{-1} can be assigned to this mode. On deuteration one expects a wavenumber shift by a factor $1/\sqrt{2}$, so that the E_u band should be found near 300 cm^{-1} in the spectrum of the deuterated crystal. In fact there is a band at 304 cm^{-1}, however with a smaller intensity. At room temperature in this spectral region a very broad and still rather intensive band is observed at 299 cm^{-1}. The intensity of this band arises partly from the E_u component of the vibration $\nu_3{}^{SnCl_6}(F_{1u})$ however, which develops into a discrete band with decreasing temperature and is shifted considerably to higher wavenumbers.

In the IR spectrum of the ordinary hydrate at helium temperatures one finds above the A_u component of the vibration $\nu_3{}^{SnCl_6}(F_{1u})$ at 333 cm^{-1} another band which has completely disappeared at CO_2 temperature already. This band is missing in the corresponding spectrum of the deuterated crystal, but the A_u-band of the $SnCl_6$-ions is considerably broadened. Its maximum shows a weak structure which might arise from two closely adjacent vibrations, which could not be resolved in the calculated ε''-spectrum however. But from a comparison of the helium temperature spectra of both crystals one must conclude that the band at 333 cm^{-1} in the spectrum of the ordinary hydrate coincides with the A_u component of the vibration $\nu_3{}^{SnCl_6}(F_{1u})$ at 304 cm^{-1} in the spectrum of the deuterated crystal. On account

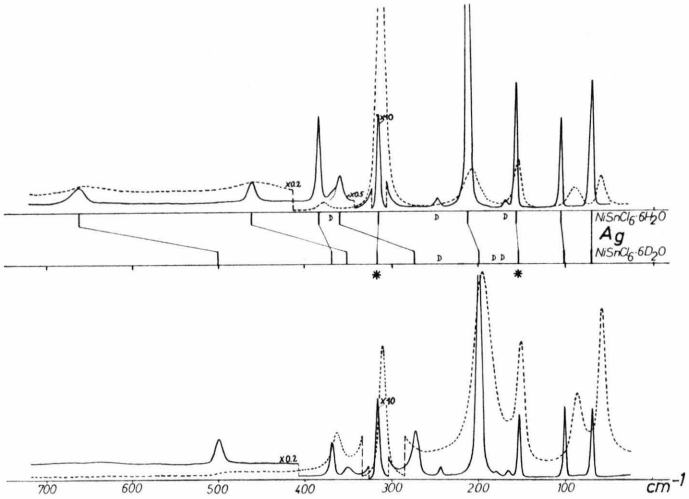

Fig. 2. Raman spectra of type A_g of $NiSnCl_6 \cdot 6\,H_2O$ and $NiSnCl_6 \cdot 6\,D_2O$ at room temperature (broken line) and at $T = 2$ K (solid line). The asterisks mark internal vibrations of the $SnCl_6^{2-}$ ion.

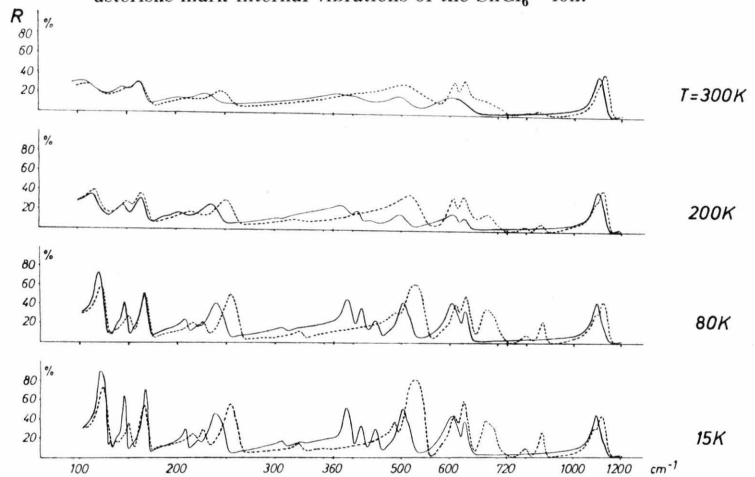

Fig. 5. IR reflection spectra of type A_2 of α-$NiSO_4 \cdot 6\,H_2O$ (broken line) and α-$NiSO_4 \cdot 6\,D_2O$ (solid line). Note change of scale at 360 cm^{-1} and at 720 cm^{-1}.

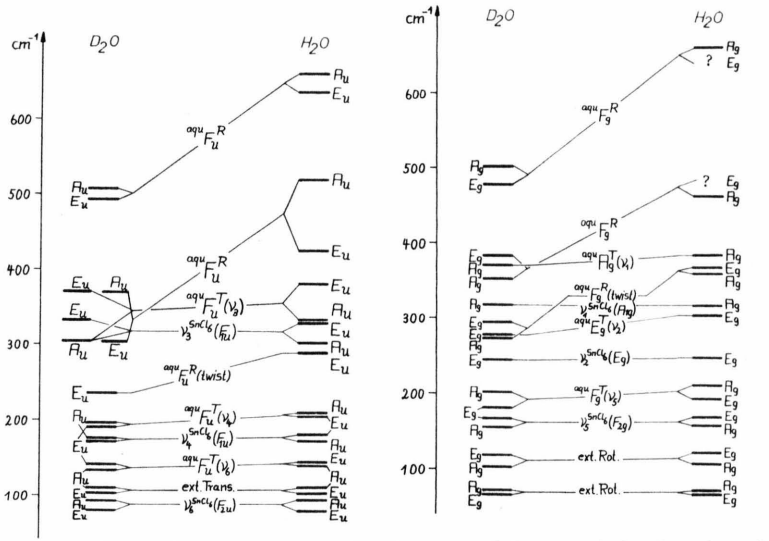

Fig. 4. Energy levels of the IR active (left part of the figure) and Raman active (right) lattice vibrations of $NiSnCl_6 \cdot 6\,H_2O$ and $NiSnCl_6 \cdot 6\,D_2O$. $^{aqu}\Gamma^{R,T}$ denotes rotatory (R) or translatory (T) normal vibrations of the "free" hydrate complex of symmetry type Γ. The assignements are given in brackets. The notation used is in accordance with [2, 14]. $\nu_i^{SnCl_6}(\Gamma)$ denotes the normal vibrations ν_i of symmetry Γ of the free $SnCl_6^{2-}$ ion according to [16].

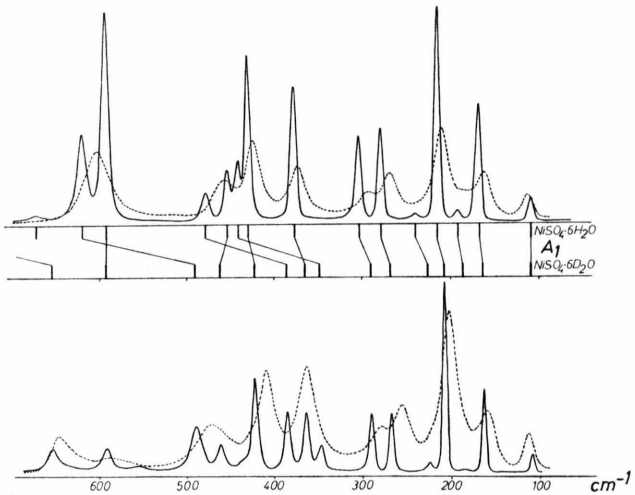

Fig. 6. Raman spectra of the A_1 vibrations of α-$NiSO_4 \cdot 6\,H_2O$ and α-$NiSO_4 \cdot 6\,D_2O$ at room temperature (broken line) and at $T = 2$ K (solid line).

Table 2. Results of the Kramers-Kronig-transformation of the spectra of Figure 3. $\tilde{\nu}$: wavenumbers of the maxima of ε''. $\Delta\tilde{\nu}$: widths of the lines of the ε''-spectrum.

$NiSnCl_6 \cdot 6 H_2O$, (A_u)								$NiSnCl_6 \cdot 6 D_2O$ (A_u)							
300 K		200 K		80 K		15 K		300 K		200 K		80 K		15 K	
$\tilde{\nu}$ [cm^{-1}]	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
88	~14	90	~10	94	4,3	96	1,6	86	15	89	8,8	93	4,4	94	2,4
		109		111	~7,5	112	2,7					110	7,2	111	2,8
140	~16	139	~13	141	5,4	142	2,4			131		133	4,8	134	2,4
166	~18	169	14	174	4,4	174	2,4	166	19,5	168	12,5	175	5,4	175	3,2
204		205	~15	209	11,2	209	5,4			194		197	11,5	197	8,8
297	14	299	11,6	304	4,7	304	3,8	296	21	297	12	303	6,6	304	5,6
				332		333	9,5								
				516	~40	519	36					369	25,5	369	24
				660	22	662	19					506	18,5	507	17,6
$NiSnCl_6 \cdot 6 H_2O$ (E_u)								$NiSnCl_6 \cdot 6 D_2O$ (E_u)							
73	~10	76	~ 8	80	4,2	81	2,4	69	~13	75	8	79	3,6	81	2
144	~13	146	9	146	3,8	146	3,8	140	~14,5	139	13,5	141	4,8	141	3,2
177	~11	178	10	181	6,4	182	~ 6					173	~ 7	173	~ 5
199	22	201	17,5	207	8,2	207	6,8	182	28	184	22	191	10,5	191	7
						290						236	~11	236	~ 8
309	33	317	~30	331	9,8	329	7,6			~320	(shoul-	331	14,5	332	12
		378		381	10	381	8				der)	371	~22	371	~22
		414	47	426	15	426	10,4	299	~80	299	~80	303	11,2	304	8,8
				636	22	638	19	474		474		494	17,6	493	17,6

Table 3. Wavenumbers $\tilde{\nu}$, line widths $\Delta\tilde{\nu}$ and assignments of the Raman lines of $NiSnCl_6 \cdot 6 H_2O$ and $NiSnCl_6 \cdot 6 D_2O$.
If not otherwise indicated, the vibrations of the free radicals are of type F_g.
\+ Present only in the form of very broad and flat raisings of the base line.
Note: In the spectrum of the deuterated crystal two more lines were found which probably are due to the valence vibrations of the HDO molecule.
($\tilde{\nu}$ = 3510 cm^{-1} (A_g, OH-stretching vibration), $\tilde{\nu}$ = 2591 cm^{-1} ($A_g + E_g$; OD-stretching vibration)).

	$NiSnCl_6 \cdot 6 H_2O$				$NiSnCl_6 \cdot 6 D_2O$				
	2 K		300 K		2 K		300 K		
	$\tilde{\nu}$ [cm^{-1}]	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	Zuordnung
A_g	3520	4	3524	40	2623	8	2628	46	
	3481	3	3490	30	2553	4	2558	22	ν_2, ν_3, H_2O, D_2O
			?		1174	8	1187	12	ν_1, D_2O
	660	18	+		499	12	+		Ni(aqu)$_6$ int. Rot.
	460	10	+		347				Ni(aqu)$_6$ int. Rot.
	382	5	377	12	368	5	363	15	Ni(aqu)$_6$ int. Trans. (A_g)
	357	8			272	8			Ni(aqu)$_6$ int. Rot.
	314	5	311	10	316	5	311	9	ν_1 $SnCl_6$
	209	5	207	20	199	7	195	21	Ni(aqu)$_6$ int. Trans.
	156	4	154	9	153	4	152	10	ν_5 $SnCl_6$
	105	4	90	16	101	4	86	16	ext. Rot.
	70	5	59	9	70	4	58	9	ext. Rot.
E_g	3527	5	+		2626	12	2639	30	
	3460	3	+		2535	4	2541	25	ν_2, ν_3, H_2O, D_2O
	1604	12	?		1184	8	1191	13	ν_1, H_2O, D_2O
	365	9	+		292	8	281	30	Ni(aqu)$_6$ in Rot.
	301	5			273	6			Ni(aqu)$_6$ int. Trans. (E_g)
	245	5	238	15	242	5	238	14	ν_2, $SnCl_6$ (E_g)
	191	5			179	5			Ni(aqu)$_6$ int. Trans.
	167	4,5	166	11	165	4,5	166	10	ν_5, $SnCl_6$
	120	7	?		116	4	95	+	ext. Rot.
	65	4	59	10	65	4,5	58	8	ext. Rot.

of this isotope effect we assign the band to the A_u component of the translatory internal vibration $\nu_3^{Ni\cdot 6aqu}(F_u)$ of the hydrate complex (compare [2]). The weak band at 381 cm^{-1} in the E_u spectrum of the ordinary hydrate can then be identified with the E_u component of the same vibration. In the spectrum of the deuterated crystal this E_u component is observed near 371 cm^{-1}.

An alternative assignment of the bands in the ν_3-region of the hydrate complex seems to be possible, which assumes that the E_u component of this vibration approximately coincides with the E_u component of the rocking mode of the complex. The change in intensity of this band could then be explained by a strong interaction of both normal coordinates in the ordinary hydrate which is lifted in the deuterated crystal. The weak band at 381 cm^{-1} in the spectrum of the ordinary hydrate however can not be explained and must be due to imperfections of the crystal or its surface. In fact the crystals of the ordinary hydrate were optically of lower quality than the deuterated crystals. The assignment of all other IR bands and of the Raman lines seem to be of less ambiguity.

b) α-$NiSO_4 \cdot 6$ aqu

The IR reflection spectra of the lattice vibrations of symmetry type A_2 and the Raman spectra of the A_1 vibrations of α-$NiSO_4 \cdot 6$ aqu are shown in Figures 5 and 6. These spectra make the common features of all other spectra of this compound sufficiently evident, so that it is unnecessary to reproduce the remaining spectra (vibrations of types B_1, B_2 and E; E Raman and IR active). They can be found in [18], together with a more complete discussion. The spectra suggest a division into two ranges:

b1) $\bar{\nu} < 350\ cm^{-1}$

In this region the line shapes and intensities in the spectra of the deuterated crystal are rather similar to those observed in the corresponding spectra of the ordinary hydrate. Between say 350 cm^{-1} and 150 cm^{-1} one expects crystal modes which arise essentially from the translatory internal vibrations ν_2, ν_4, ν_5, and ν_6 of the hydrate complex with line shifts as a consequence of deuteration of the order 10 to 15 cm^{-1}. Below say 150 cm^{-1} one expects only external lattice vibrations of the crystal, which only show an isotope shift of a few wavenumbers. All the IR and Raman lines observed in the region below 330 cm^{-1} are listed in Table 4. We shall not try here to give a detailed assignment of the lines observed in this spectral region.

b2) $\bar{\nu} > 350\ cm^{-1}$

Between roughly 900 and 350 cm^{-1} one expects besides the modes $\nu_4(613; F_2)$ and $\nu_2(451; E)$ of the sulfate ion the predominantly rotatory internal vibrations of the hydrate complex and in the region near 400 cm^{-1} the translatory vibrations $\nu_1(A_g)$ and $\nu_3(F_u)$ of the complex. On deuteration the ro-

Table 4. Wavenumbers of IR and Raman lines found in the spectra of α-$NiSO_4 \cdot 6\ H_2O$ and α-$NiSO_4 \cdot 6\ D_2O$ below 330 cm^{-1} at helium temperature. In the IR region no measurements were made below 80 cm^{-1}. The B_1-lines marked with an asterisk are possibly due to B_2 vibrations which occur in the B_1 spectrum because of imperfect polarisation..

A_1		B_1		B_2		*E* (Raman)		*E* (UR)		A_2	
H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
306	289	327	314	301	286	298	284	298	283	326	308
278	267	302 *	286	276	260	283	269	283	269	251	237
241	226	274 *	260	253	239	265	259			227	222
217	206	252 *	238	235	220	247	236	246	237	217	208
194	185	218	211	212	198	208	200	207	201	164	166
169	162	211 *	198	148	147	197	189			150	144
111	108	169	168			177	172	179	173	137	132
		160	155			164	164	166	163	121	119
		148 *	147			139	137	141	136		
		139	139			133	132				
		104	106			106	105	103	101		
		69	69			96	93				
						85	85	87	86		
						79	78				
						68	68				
						55	55				

Table 5. Results of the Kramers-Kronig transformation of the spectra of Figure 5. Same notation as in Table 2.

		$NiSO_4 \cdot 6H_2O$						$NiSO_4 \cdot 6D_2O$					
				A_2						A_2			
	300 K	200 K	80 K	15 K	300 K		200 K	80 K		15 K			
$\tilde{\nu}$ [cm^{-1}]	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
114		116	~16,5	121	7,8			~105		112	18	117	4,2	119	1,5
				137								131		132	
162		152	~13	151	7,8	150	5,6	145	~11	149	~10	146	3,8	144	2,4
		163	11	166	4,8	164	4,2	159	~16	162	10	166	4,2	166	3
~216		220	~22	217	~8	217	~7	204		205	~16	208	6	208	~4
				227	~8	227	~7					222		~222	
247	19,5	250	14	253	6,5	251	6,5	231	~36	234	18	238	9	237	6,8
		324		327	~7	326	~6					310		308	
						345								~325	
				489	18,5	489	10			372	26	386	14	384	8,8
497	90	504	52	519	15,2	514	6,8			406	19	416	11,5	416	10,5
												446	16	446	13,5
607	16	607	15	610	14,5	607	12	592	64	600	44	597		596	24
626	~17	624	~18	626	14,5	622	12			628	19	627	11	627	10
		666	~40	667	17	668	~14	490	64	494	40	498	15,5	498	12,5
		~796		801	~32	797	22								
		860	27	865	19	860	17								
		?	(shoulder)	~1093	(shoulder)	~1090	(shoulder)					1091	20,5	1090	19
1114		1114	?	1116	?	1108	?						?	(shoulder)	

tatory modes are shifted into the range of the internal vibrations of the sulfate ion or across this range to lower wavenumbers. Because of an interaction between the internal modes of the hydrate complex (especially the rotatory ones) and the internal modes of the SO_4 ions, in the spectra of the deuterated crystal the intensities of most lines above 350 cm^{-1} are changed, as compared to the corresponding lines in the spectra of the ordinary hydrate, so that it is difficult to make a unique correlation. The reflection spectra of Fig. 5 can serve as an example (see also Table 5). The band below 700 cm^{-1} in the low temperature spectrum of $NiSO_4 \cdot 6H_2O$ is obviously shifted to 500 cm^{-1} in the spectrum of the deuterated crystal. On account of the large transition dipole moment and because of the large shift $(1/\sqrt{2})$ they can be assigned to the two A_2 components of the rocking mode of type F_u in the "free" hydrate complex. The two bands at 797 and 860 wavenumbers may then arise from the corresponding E_g-vibration. In the spectrum of the deuterated crystal they can be expected in the range of the double band of the sulfate ion near 600 cm^{-1} where they cannot be separated. The lineshape of the sulfate doublet, however, and its dependence on temperature is evidently considerably different in the two compounds. It is also interesting to note

Table 6. Wavenumbers and assignments of the lines in the A_1 Raman spectrum of α-$NiSO_4 \cdot 6H_2O$ and α-$NiSO_4 \cdot 6D_2O$ observed at $T = 2$ K. For comparison the wavenumbers of the corresponding vibrations as observed in $NiSnCl_6 \cdot 6$ aqu are included in square brackets.

Assignment of the vibrations of the free $(Ni \cdot 6\,aqu)^{2+}$-ion		$-NiSO_4 \cdot 6H_2O$		$-NiSO_4 \cdot 6D_2O$	
"rocking-modes"	(F_g)	?		613	
	(F_u)	621		488	
($\nu_4 SO_4$ (613; F_2)		594		592)	
"wagging-modes"	(F_u)	480		384	
	(F_g)	442		347	
ν_3	(F_u)	?		?	
($\nu_2 SO_4$ (451; E)		454 431		461 421	
ν_1	(A_g)	378	[382]	363	[368]
ν_2	(E_g)	305 280	[301]	289 267	[273]
ν_4	(F_u)	241	[209 207]	224	[197 191]
ν_5	(F_g)	217	[167 156]	206	[165 153]
ν_6	(F_u)	194	[146 142]	185	[141 134]
external lattice modes		169 111		162 108	

that even the reflection band near 1100 cm^{-1} (ν_3, SO_4^{--}) changes its shape on deuteration.

This example may elucidate why an unambiguous interpretation of all spectra observed in α-$NiSO_4 \cdot 6$ aqu is not possible. Only the A_1 Raman spectrum offers a chance for a thorough interpretation and can therefore be used as a guide to survey the main features of the spectra. The assignments of all A_1 lines observed are given in Table 5. The underlying assumption is, that crystal vibrations which arise from IR active translatory internal vibrations of the crystal give rise only to weak lines. It is apparent from Table 5, that in α-$NiSO_4 \cdot 6$ aqu the vibrations of the hydrate complex are generally observed at higher wavenumbers than in $NiSnCl_6 \cdot 6$ aqu. This can be explained by the smaller dimension of the complex and by the stronger hydrogen bonding which also leads to larger shifts of the valence vibrations of the water molecules towards smaller wavenumbers in the sulfate than in $NiSnCl_6 \cdot 6$ aqu.

An attempt to achieve a coherent interpretation of all the spectra starting from the assignments given above shows that there must be a larger splitting between the different crystal modes which arise from the same interval vibration of the "free" hydrate complex, as compared to the case of $NiSnCl_6 \cdot 6$ aqu. The rotatory modes show splittings of the order of 100 wavenumbers and the translatory modes show splittings of the order of 30 wavenumbers. This can partly be due to a much larger site group splitting than is expected from the nearly regularly octahedral oxygen positions in the hydrate complex. If the (unknown) proton positions were included, the complex in the crystal would probably show rather large deviations from the T_h symmetry of the unperturbed complex.

Temperature Dependence of the Spectra and Anharmonicity of the Lattice Potential

The spectroscopical data presented here as well as in [19] and [20] show that the spectra of hydrated crystals with molecular structural units depend much stronger on temperature in the region between room temperature and liquid helium temperature than the spectra of comparable anhydrous ionic crystals. This temperature dependence is observed not only on the line widths of crystal modes arising from internal vibrations of the molecular anions. The predominantly rotatory internal vibrations of the hydrate complex show the most pronounced effect. In the room temperature spectra they appear in most cases as very broad and flat raisings only. The effects are somewhat smaller in the predominantly translatory internal vibrations. In the case of internal vibrations of the anions this temperature dependence seems to be determined for a large part by admixtures of normal vibrations of the free metal hydrate complex for which a strongly anharmonic potential can be assumed (see below). If the internal vibrations of the anions lie in the same wavenumber range as the internal vibrations of the hydrate complexes, this effect can lead to a nearly uniform temperature dependence of the whole spectrum in this region (see e. g. Figure 1, $E \perp z$).

The external lattice vibrations are governed by a potential constructed from short range forces and long range Coulomb forces which in accordance with all experience can be described relatively well by using the harmonic approximation. For hydrated crystals in addition to a potential of the type just described a further contribution is present which includes the hydrogen bonding and the electrostatic and van der Waals bonding of the water molecules in the crystal. The hydrogen bonding can be described in terms of the empirical Lippincott-Schroeder model [21] and the bonding of the water molecules in the hydrate complex can be described following Mathieu [22]. Both models are briefly discussed below. They are certainly of limited significance, however sufficiently precise quantum mechanical calculations do not exist or are too involved for the present case (l. c. [23, 24]).

The Lippincott-Schroeder model was used to calculate the contribution of the hydrogen bondings to the potential of the totally symmetric stretching vibration and to the rotatory internal vibrations of the hydrate complex. This one-dimensional model of hydrogen bonding starts from the expression

$$V = D(1 - \exp\{-n \cdot \Delta r^2/2\, r\})$$

used for describing the O – H bond as well as the highly stretched and weak H ... O bond in an $X_1O - H \ldots OX_2$ configuration. D and n are constants which can be determined from experimental data (see [21]). $\Delta r = r - r_0$, r_0 being the O – H bond length of a free water molecule. For the interaction between both oxygen atoms the potential of Born-Mayer type $V' = A\, e^{-bR} - B/R^m$ is chosen. We used the conditions for a stable equilibrium to establish

equations from which the O – H distance r and the energy of the hydrogen bonding can be calculated as a function of the O . . . O distance R. For R being constant, i. e. for a constant V', the bond energy only depends on the distances r_{O-H} and $r_{H...O}$. This fact was used [25] as a starting point for the extension of the model to allow for non linear hydrogen bonds which permits a calculation of the hydrogen bond contribution to the potential of rocking, wagging, and twisting modes of the water molecules. A bending of the hydrogen bonds also occurs, when the water molecule is performing translatory motions along its C_2 axis. The bonds are assumed to be linear when the molecule is in its equilibrium position. In all calculations allowance was made for the fact that for a given bond angle $\varphi < 180^\circ$ of the O – H . . . O bond the potential minimum occurs at an O – H distance $r(\varphi) < r(180^\circ)$. To simplify the problem we assumed that the water molecule as well as the two ligand O-atoms lie in one plane and that the angle between the lines connecting the O-atom of the water molecule and the ligand O-atoms is equal to the natural bond angle of the water molecule.

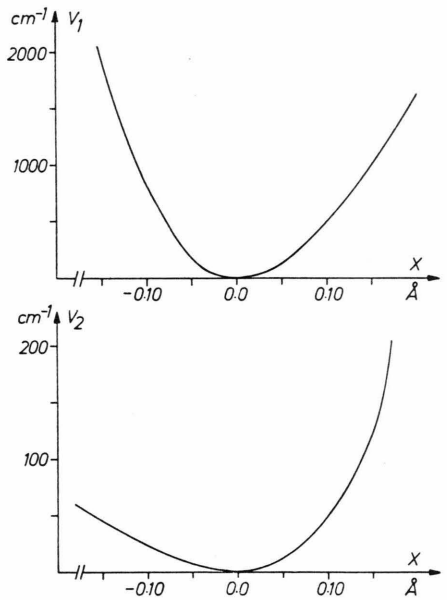

Fig. 7. Potential for a translatory motion of a water molecule along its C_2 axis within the frame of the Ni^{2+} ion and the two O atoms to which the molecule is hydrogen bonded. X is the distance of the center of gravity of the water molecule from the equilibrium position. V_1 and V_2 are the contributions from the bonding of the water molecule inside the hydrate complex and from the hydrogen bonds respectively, as discussed in the text. The O – H . . . O bond lengths and the Ni – OH_2 distance are assumed to be 2.7 Å and 2.0 Å respectively.

The result of this calculation of the hydrogen bond contribution V_2 to the potential of the stretching mode of a rigid water molecule in the hydrate complex is plotted in Figure 7.

The same hydrogen bond potential contributes to the potential energy of external lattice vibrations consisting of motions of the hydrate complexes and the molecular anions as rigid units against each other with amplitudes of the order of 0.1 Å as a rough estimate for the thermal excitation of these vibrations at room temperature [17]. Now the difference in the hydrogen bond contribution to the potential energy between two positions of a water molecule being ± 0.1 Å apart from the equilibrium position is about 10% of the observed transition energy of the totally symmetric stretching vibration of the complex as Fig. 7 shows. The hypothesis established above concerning the anharmonicity of the hydrogen bond contribution to the lattice potential therefore seems to be supported by the model.

The bonding of the water molecules inside the hydrate complex can be investigated best by considering the potential, that governs the motion of a water molecule in radial direction. This gives an estimate of the potential of the totally symmetric stretching vibration if one is allowed to neglect all interactions of the different water molecules of the same complex other than the dipole-dipole forces. The expression for this potential used by Mathieu, which only includes contributions for which a numerical estimate is possible, takes into account the different contributions to the electrostatic energy of a water dipole in the hydrate complex [26] and the van der Waals energy and a repulsive potential between the water molecules and the cation. The potential V_1 calculated from this expression for the nickel complex is plotted in Figure 7. As in the case of the hydrogen bond it is strongly anharmonic already for realistic values of the vibration amplitude, and although the "soft" branch of this potential coincides with the stiff branch of the hydrogen band contribution, there is no compensation of the anharmonic terms of both contributions.

In conclusion one may say that the simple potential models considered support the suggestion that the temperature dependence of the spectra of hydrated crystals is caused by the anharmonicity of the potential by which the water molecules are bound inside of the hydrate complexes and to the residual lattice, although the quantitative conclusions that

can be drawn from the model may be of limited value.

The same model was used to calculate the potential for the librational modes of the water molecules, which consist essentially of the hydrogen bond contribution and the contribution of the permanent dipole moment of the water molecules in the electric field of the metal ion. This potential turned out to be approximately harmonic up to amplitudes as large as 10 degrees (which are observed by NMR methods; see e. g. [27]). This is in contradiction to the experimental observation that especially the rotatory internal modes of the hydrate complexes exhibit a pronounced temperature dependence of their line widths. The explanation can be given by the fact that the potential energy of the librational modes depends strongly on the position of the water molecule, i. e. the distance of the center of gravity to the central metalion and the other water molecules of the complex, which introduces an anharmonic coupling to the translatory modes of the hydrate complex. The dependence of the dipole contribution to the libration potential on the particle position can be used to estimate the value of the line width of these vibrations at room temperature, when the totally symmetric stretching vibration of the complex is thermally excited. The restoring force F acting on a dipole in a non-equilibrium position in the distance r from a point charge is proportional to r^2. If Θ_i is the moment of inertia for the libration concerned, we have $\hbar\,\omega_i = \hbar\,\sqrt{F/\Theta_i} \sim 1/r$. If an amplitude of 0.1 Å is assumed for the totally symmetric translatory vibration and an average value of 600 wavenumbers for $\hbar\,\omega_i$, the radius of the complex being 2 Å, we get a difference of 60 wavenumbers in potential energy between the two extreme positions of the water molecule where the probability of presence of the oscillating particle in its first excited state is maximum. This estimate is of interest only with respect to the order of magnitude, which is in accordance however with the observed values of the line widths of the librational modes at room temperature (see Tables 2 and 5).

As a consequence of the anharmonicity of the lattice potential the linewidths $\Delta\bar{\nu}$ depend according to theory (see [4] for references) in the high-temperature approximation ($\hbar\,\omega_i \ll k\,T$) linearly on T if the cubic contributions to anharmonicity predominate or quadratic if the quartic contributions are most significant. Plots of the observed linewidths (see Tables 2 and 5) of transitions with $\bar{\nu} \leqq 150\ \mathrm{cm}^{-1}$ ($\hbar\,\omega_i \leqq k\,T$) over the temperature show exponents of T between 0.9 and 1.12 in the high-temperature region, independent of the assignment (external lattice mode, $SnCl_6^{--}$-mode, internal translation of the hydrate complex). This fact demonstrates that at least at low frequencies three-phonon processes are dominiant in these crystals and it excludes reorientation processes of any kind as the source of linewidth (e. g. [28]). In this latter case $\Delta\bar{\nu}$ grows exponentially on temperature with an Arrhenius type dependence in clear contradiction to the results presented here. The observed preponderance of cubic anharmonicity in the lattice potential is to be expected because of the asymmetry of the calculated potential in the hydrate complex (Fig. 7), where obviously the cubic term far outweights the quartic contribution.

Conclusion

The IR and Raman spectra of the ordinary tin chloride hydrate and the deuterated crystal could be interpreted using a model of isolated ($SnCl_6^{2-}$) and ($Ni^{2+}\cdot 6$ aqu) complexes. All bands predicted by group theory could be observed so that it was possible for the first time to determine the energies of all internal vibrational states of an octahedral metal hydrate complex. This completes the results known from previous work by other authors. Comparison with other measurements and especially with the results obtained from α-$NiSO_4\cdot 6$ aqu shows, however, that the energy of these vibrations depends much stronger on the special crystal lattice than it is observed for the internal vibrations of molecular anions with strong intramolecular covalent bonding. Therefore it is meaningful only to some extent to discuss the properties of metal hydrate complexes independently of the host lattice by regarding them as free molecular ions.

The strong temperature dependence of the spectra, which characterizes ionic-crystals with hydrate complexes could be correlated qualitatively with the anharmonicity of the potential in the complex. This demonstrates that the presence of hydrate complexes in a crystal introduces additional anharmonicity which is effective for all modes of the crystal to a degree depending on the coupling with the complex.

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Zur Analyse der Rotationsspektren in torsionsangeregten Zuständen von Molekülen mit zwei Methylgruppen

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A Contribution to the Analysis of Rotational Spectra in Torsional Excited States of Molecules with two Methyl Tops

An analysis of the rotational spectra in torsional excited states is given for propane, dimethylsilane and dimethylsulfide. The analysis is based on the Hamiltonian for the quasi-rigid model. The potential barrier V_3 and one additional potential coefficient V'_{12} were determined. The splitting within the multipletts could be reproduced, but not the spacing between them.

Seit geraumer Zeit ist die Analyse der Torsionsfeinstruktur in Rotationsspektren eine gute Methode zur Bestimmung von Hinderungspotentialen der internen Rotation oder Torsion bei Molekülen mit einer oder zwei Methylgruppen. Meist wird jedoch nur der erste Koeffizient in der Fourier-Entwicklung ermittelt, da die Bestimmung höherer Koeffizienten zusätzliche Informationen aus den Rotationsspektren angeregter Torsionszustände benötigt.

Hier berichten wir über die Bestimmung eines solchen Koeffizienten aus den Rotationsspektren von Propan, $(CH_3)_2CH_2$, Dimethylsilan $(CH_3)_2SiH_2$, und Dimethylsulfid, $(CH_3)_2S$.

Die verwendeten Übergänge sind in den Tab. 1 bis 3 aufgeführt. Die Linienfrequenzen von Propan sind von Hirota et al. [1], die von Dimethylsulfid von Hayashi [2]. Die Spektren der torsionsangeregten Zustände von Dimethylsilan wurden im Laufe dieser Arbeit gemessen und zugeordnet.

Der Analyse liegt ein Modell zugrunde, bei dem der Molekülrumpf und die Methylgruppen als starr angenommen werden. Die einzigen beiden inneren Freiheitsgrade sind die der Torsion. Die äußeren Freiheitsgrade sind die der Rotation.

Der Hamilton-Operator für dieses Molekülmodell lautet [3]:

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