

STUDY OF THE VIBRATIONAL SPECTRA OF NATROLITE

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ABSTRACT

The vibrational spectra of natrolite from Těchlovice, Bohemia, were measured in the infrared ($200\text{--}4000\text{ cm}^{-1}$) and the far-infrared ($40\text{--}400\text{ cm}^{-1}$) regions; the infrared reflectance ($200\text{--}1400\text{ cm}^{-1}$) and Raman scattering ($50\text{--}4000\text{ cm}^{-1}$) spectra of the polycrystalline material were also measured. The Shimanouchi (1963) GCCC, BGLZ and LSMA programs were used to calculate the force constants and vibrational frequencies. The KKK-1 program (Kroupa & Pelzelt 1982) was used to calculate the dispersion curves of the optical constants. The bands in the spectra can be assigned to the vibrations of the individual bonds and structural groups on the basis of theoretical calculations and literature data.

Keywords: complex vibrational spectra, natrolite, Těchlovice, Bohemia.

SOMMAIRE

On a mesuré les spectres de vibration de la natrolite de Těchlovice (Bohème) dans l'infra-rouge ($200\text{--}4000\text{ cm}^{-1}$) et l'infra-rouge lointain ($40\text{--}400\text{ cm}^{-1}$), ainsi que les spectres de réflectance infra-rouge ($200\text{--}1400\text{ cm}^{-1}$) et de dispersion Raman ($50\text{--}4000\text{ cm}^{-1}$), sur matériau polycristallin. Les programmes GCCC, BGLZ et LSMA de Shimanouchi (1963) ont servi à calculer les constantes de force et les fréquences de vibration, tandis que le logiciel KKK-1 (Kroupa & Pelzelt 1982) permet de calculer les courbes de dispersion des constantes optiques. Les bandes des spectres sont attribuées aux vibrations des liaisons individuelles et des groupes structuraux à la lumière des prédictions théoriques et des données publiées.

(Traduit par la Rédaction)

Mots-clés: spectres de vibrations complexes, natrolite, Těchlovice, Bohème.

INTRODUCTION

Three principal optical methods can be used to measure the vibrational spectra of crystals: 1) the absorption of infrared radiation, 2) the reflectance of infrared radiation, and 3) the Raman scattering of visible radiation. These methods are complementary both in experimental technique and in the use of selection rules (Poulet & Mathieu 1973). Infrared-absorption spectra in the far-infrared and infrared region are suitable especially for the determination

of vibrations of water molecules, hydroxyl groups and local bonds in the structure of minerals. To get approximate information about the vibrations of crystalline substances with a centre of symmetry, the infrared spectra must be complemented by their necessary supplement *i.e.*, the study of Raman spectra (selection rules). Reflection spectra yield information about the vibrations of structural groups and bonds and are suitable especially for calculation of the dispersion of optical constants (Poulet & Mathieu 1973, Turrell 1972). These conclusions can be derived from the theory of vibration spectra, which was described in many recent publications (Poulet & Mathieu 1973, Turrell 1972, Ross 1972). Infrared-absorption spectra in the middle region ($400\text{--}4000\text{ cm}^{-1}$) were published in several papers (Breck 1974, Flanigen *et al.* 1971, Farmer 1974), in the $200\text{--}4000\text{ cm}^{-1}$ wavenumber region by Pechar & Rykl (1980) and in the far infrared region by Pechar (1982). The Raman and reflection spectra of polycrystalline natrolite have not been published yet (to the authors' knowledge). The aim of this paper is to point out, in a first approximation using natrolite as an example, what information can be obtained by an integrated study of these types of vibration spectra. The Shimanouchi (1963) GCCC, BGLZ and LSMA programs served to calculate the force constants and vibrational frequencies.

EXPERIMENTAL

The infrared-absorption spectra of a natural natrolite with an ideal crystallochemical formula of $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ (locality: Těchlovice, Bohemia; host rock: basalt) were measured in the wavenumber region $200\text{--}4000\text{ cm}^{-1}$ (Pechar & Rykl 1980) on a double-beam Perkin-Elmer 325 spectrometer. Samples of the crystalline material were prepared in pellet form with KBr (1:40); the spectra were measured at standard temperature and pressure (Fig. 1).

The infrared-absorption spectra in the far-infrared region $40\text{--}400\text{ cm}^{-1}$ (Pechar 1982) were measured using a Beckman FS-720 infrared interferometer (Fig. 2). Samples were prepared in polyethylene foil (1:20) at 200°C and measured *in vacuo* (1.3 Pa) at standard temperature. The spectra were evaluated by the Fourier method on computer (IBM 370).

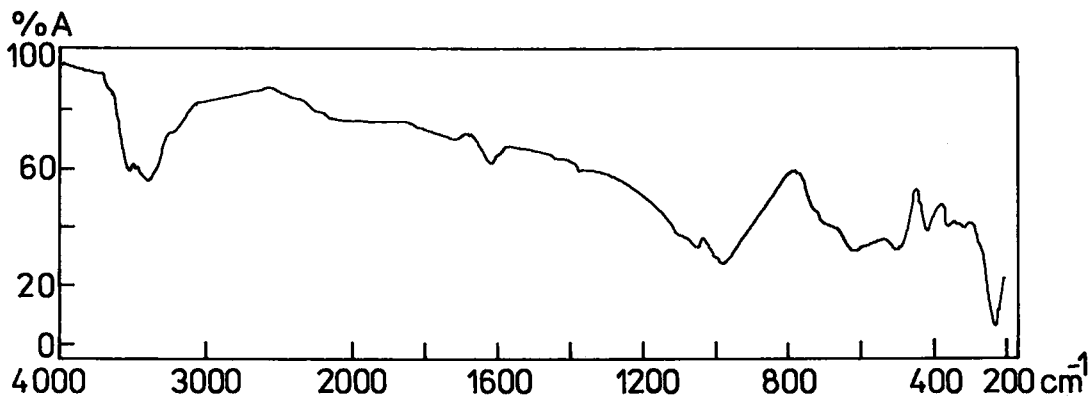


FIG. 1. Infrared-absorption spectrum ($200 - 4000 \text{ cm}^{-1}$) of natrolite.

The reflectance infrared spectra in the wavenumber range $200 - 1400 \text{ cm}^{-1}$ were measured using a Perkin-Elmer 325 spectrometer, at standard temperature and pressure (Fig. 3). Samples were prepared as optically polished crystals of natrolite (prepared by Mr. J. Baxa, Or' Research Institute, Prague). Reflectance (%R) was measured in steps

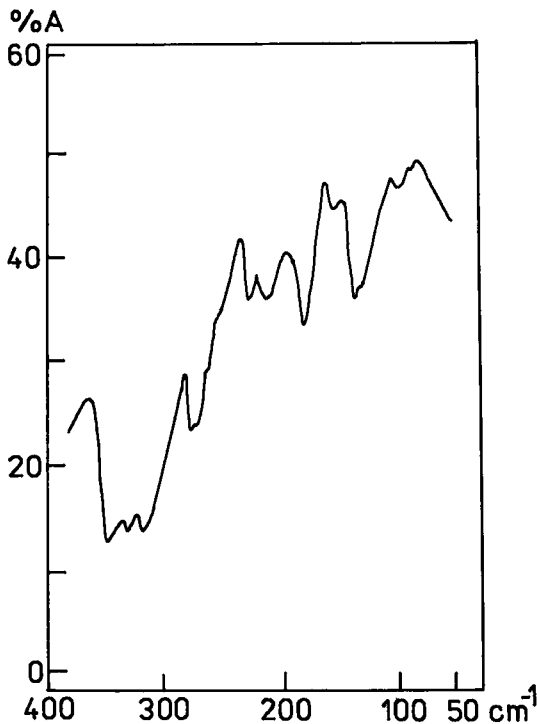


FIG. 2. Far-infrared spectrum ($40 - 400 \text{ cm}^{-1}$) of natrolite.

of 5 cm^{-1} relative to an Al mirror, and the data were treated by the KKK-1 program (Kroupa & Pelzelt 1982) for computation (IBM 370) of the dispersion curves of index of refraction and both components of the dielectric permittivity (Figs. 4-6).

The Raman scattering spectra of the polycrystalline material were measured on a SPEX 14018 laser spectrometer ($\lambda_{\text{Ar}^+} = 514.5 \text{ nm}$) at standard temperature and pressure in the wavenumber region $50 - 3600 \text{ cm}^{-1}$ (Fig. 7). Samples were prepared for measurement by cementing the crystals to a quartz rod.

The results of a quantitative chemical analysis of the natrolite sample are listed in Table 1. Table 2 provides an evaluation of all the vibrational spectra studied and the results of a calculation of the theoretical frequencies and force constants of the bands of natrolite. The group representation of the vibration of natrolite are:

$$\Gamma_{\text{vib}} = 120 A_1(\text{IR}, \text{R}) + 120 A_2(\text{R}) + 120 B_1(\text{IR}, \text{R}) + 120 B_2(\text{IR}, \text{R})$$

DISCUSSION

All the spectra studied yielded readily distinguishable vibrational bands with a relatively low background. The precision of the measurement of wavenumber of the individual bands in all the spectra is $\pm 2 - 5 \text{ cm}^{-1}$.

The spectra studied can be separated into three groups according to the range of wavenumbers measured: 1) $1400 - 3600 \text{ cm}^{-1}$: infrared-absorption spectra in the medium region and Raman-scattering spectra; 2) $200 - 1400 \text{ cm}^{-1}$: infrared-absorption spectra in the medium region, part of the far-infrared absorption spectra, reflectance-infrared spectra and Raman-scattering spectra, and 3) $40 - 200 \text{ cm}^{-1}$:

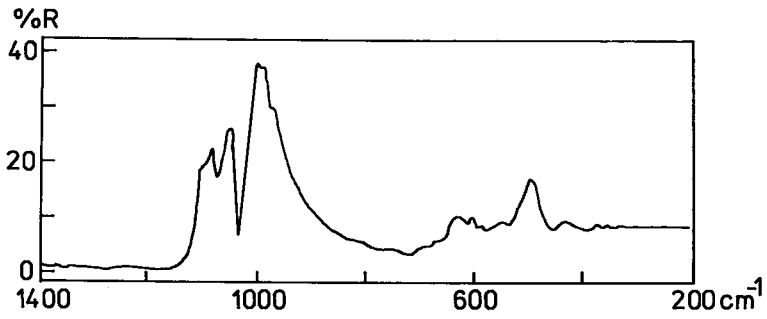
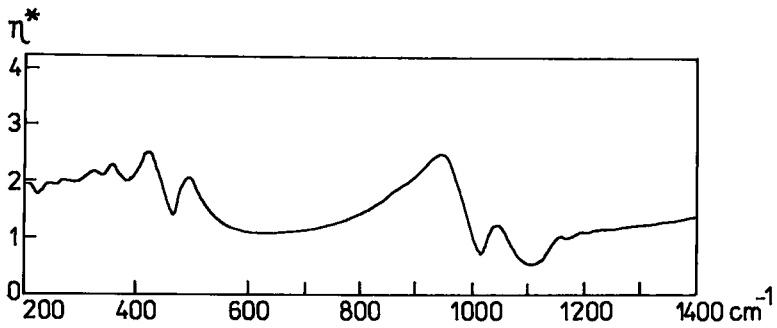
FIG. 3. Reflectance infrared spectrum ($200 - 1400 \text{ cm}^{-1}$) of natrolite.

FIG. 4. Dispersion curve of the index of refraction of natrolite.

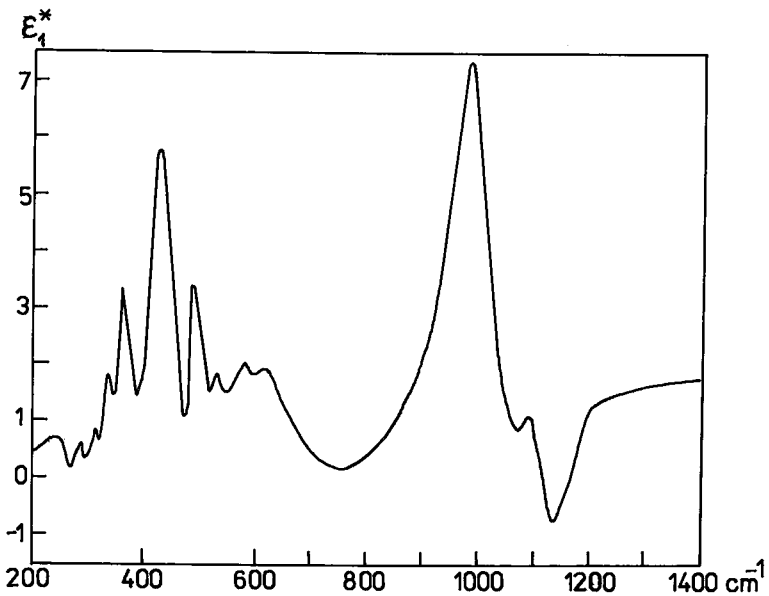


FIG. 5. Dispersion curve of the real part of dielectric permittivity.

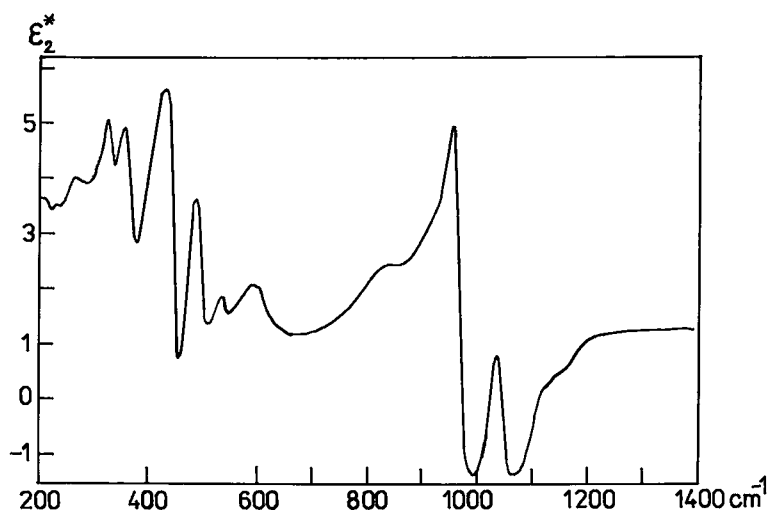


FIG. 6. Dispersion curve of the imaginary part of dielectric permittivity.

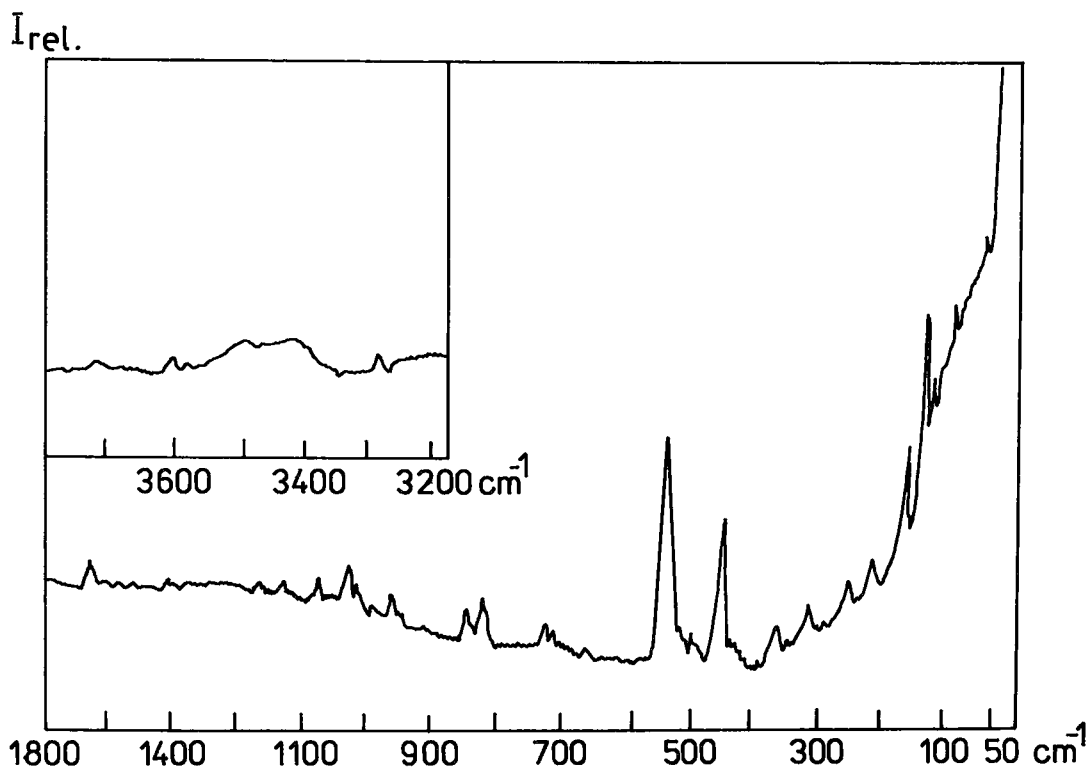


FIG. 7. Raman-scattering spectrum ($50 - 3600 \text{ cm}^{-1}$) of the polycrystalline sample of natrolite.

TABLE 1. CHEMICAL COMPOSITION OF NATROLITE FROM TĚCHLOVICE, BOHEMIA

SiO ₂	wt. %	44.66	Crystallochemical formula: (Na _{1.440} K _{0.43} Ca _{1.45})
TiO ₂		0.002	
Al ₂ O ₃		26.59	(Al _{1.632} Fe _{0.004} Mg _{0.008} Si _{2.316} P _{0.15})
Fe ₂ O ₃ *		0.013	Ti _{0.008} O _{8.0} · 15.98 H ₂ O
MnO		0.002	
MgO		0.012	
CaO		2.66	
Na ₂ O		14.20	Analyst: Ing. L. Minařík.
K ₂ O		0.74	Institute of Geology and Geo-
P ₂ O ₅		0.14	technics ČSAV
2H ₂ O		10.92	
Total		99.94	* Total iron expressed as Fe ₂ O ₃ .

far-infrared-absorption spectra and Raman-scattering spectra.

Bands of the antisymmetrical and symmetrical vibration of hydroxyl groups lie in the region 3300 – 3610 cm⁻¹. They have a very strong intensity in

the IR spectra and a low intensity in the Raman spectra. The shift of this vibration relative to the wavenumber of the same vibration for water vapor indicates the presence of hydrogen bonds (Hamilton & Ibers 1968); interatomic O . . . O distances can be determined graphically for these bonds (Fig. 8).

The H–O–H bending vibration lies at a wavenumber of 1610 – 1625 cm⁻¹, with a medium intensity in the infrared-absorption spectrum and a low intensity in the Raman-scattering spectrum.

The infrared-absorption spectrum in the medium region, the reflectance spectrum and the Raman spectrum contain bands of the antisymmetric stretching vibration of the tetrahedral T–O bonds (T = Al, Si), with a wavenumber range of 960 – 1055 cm⁻¹. These bands have a high intensity in the infrared-

TABLE 2. EVALUATION OF VIBRATIONAL SPECTRA OF NATROLITE AND COMPARISON WITH CALCULATED FREQUENCIES AND FORCE CONSTANTS

Type of vibration†	Infrared absorption medium range	Far-infrared absorption	Infrared reflection	Raman	Theoretical frequencies	Force constants*
O–H stretching	3310–3515 VS	-	-	3300–3610 W	3656	7.793
H ₂ O bending	1625 m	-	-	1610 VW	1653	0.105 0.252 0.768
External π O ₄	1110 W	-	1095 S TO 1085 S LO 1185 W LO 1210 W LO 1285 W LO 1310 W LO	1080 VW	-	-
Antisymmetrical stretching	1055 VW 975 S	-	1005 VS TO 990 VS TO 1060 S TO 965 VS LO 985 VS LO 1050 S LO	1030 W 960 W	988 896	Si–O 5.417 Al–O 3.024
Bending O–T–O	420 W	400 S	430 W	420 VW	410 420 440	2.6508 1.2356 1.0603
Symmetrical stretching	-	-	630 VW TO 610 W LO 635 W LO	840–810 W 700 VW	780 720	2.2385 2.8549
Libration of the H ₂ O	620 W 590 m 480 m	-	495 m TO 540 VW TO 600 W TO 490 S LO 540 W LO 580 W LO	525 S 485 VW	470 590 625	0.451 0.172 0.130 0.230
"Pore opening"	360 W	365 VS 348 W	365 W TO	350 W	372	0–0 0.1178
Translational H ₂ O	315 W	330 m	330 W TO 346 W TO 346 W LO	320 W 295 W	-	-
Optical mode of lattice	220 m	228 W 218 W 110 W 98 VW	225 W TO 220 W LO	230 W 109 m 95 W	-	-
Translational Ca–O	-	278 m 264 VW	-	268 VW	264	0.0363
Na–H ₂ O	-	136 VS 130 VW	-	135 VS	-	-
Translational Na–O	-	186 S 168 W	-	198 m 160 VS	190	0.0177

VS very strong, S strong, m medium, W weak, VW very weak; LO longitudinal mode, TO transversal mode; π represents Al, Si. Observed and calculated frequencies expressed in wavenumbers (cm⁻¹), force constants in N m⁻¹ × 10² (mdyn/Å).

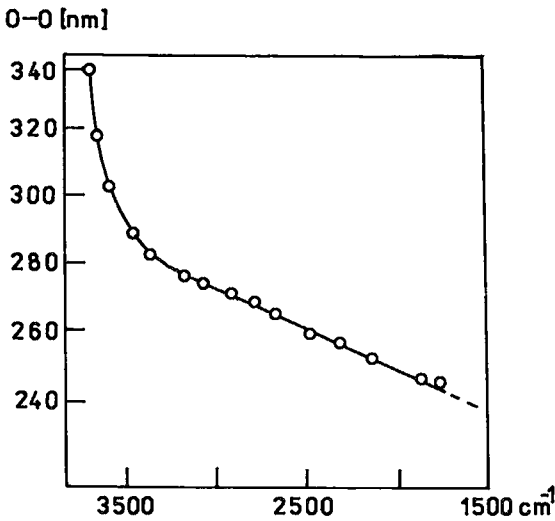


FIG. 8. Correlation between frequency shift of stretching vibration of the hydroxyl group and the equilibrium O-H . . . O distance of the hydrogen bonds (Hamilton & Ibers 1968).

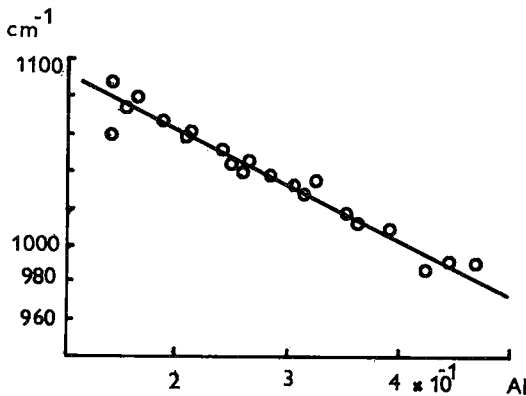


FIG. 9. Value of the Al atoms in structure of zeolites as a function of frequency shift of the stretching vibration of Si(Al)-O bonds (Breck 1974).

absorption and reflectance spectra and a low intensity in the Raman spectra. The shift of this vibration relative to the same vibration for the isolated Si-O bond indicates the value of the Al atoms in the natrolite structure; this can be determined graphically (Fig. 9) for these bonds (Breck 1974).

All the spectra except infrared absorption and far-infrared absorption contain bands of symmetrical stretching vibrations of Si(Al)-O bonds. These bands

can be found in the wavenumber region 610 - 840 cm^{-1} (Flanigen *et al.* 1971, Pechar & Rykl 1980).

The libration bands of the water molecule around the *a* and *c* axes of this molecule lie at 480 - 620 cm^{-1} in all the spectra (except far-infrared) with low intensity (Pechar *et al.* 1982). The bending vibration of the tetrahedral bonds O-Si(Al)-O corresponds to bands at a wavenumber in the range 410-435 cm^{-1} (Pechar & Rykl 1980). The "pore opening" (Breck 1974) vibration of bonds between the oxygen rings corresponds to bands in the range 348 - 465 cm^{-1} . The translational mode of the water molecules corresponds to bands in the range 292 - 346 cm^{-1} (Pechar *et al.* 1982).

The optical mode of the lattice corresponds to bands in the range 218 - 230 cm^{-1} (Poulet & Mathieu 1973). Bands of varying intensity, assigned to the Ca-O translational vibration, can be found at 263 - 278 cm^{-1} (Exarhos *et al.* 1974, Brodskii *et al.* 1973).

The bands of the translational mode of the Na-O bonds can be found in the far-infrared spectra and Raman spectra in the wavenumber range 168-198 cm^{-1} , with varying intensity (Exarhos *et al.* 1974, Brodskii *et al.* 1973). Bands with a wavenumber lower than 160 cm^{-1} can be assigned to the vibration of the cation-water complex and to the translational mode of the lattice.

CONCLUSIONS

Study of the complex vibration spectra of crystalline substances rapidly yields information on the symmetry and dynamics of the crystal lattice and on the dispersion of the optical constants in the whole region of measured frequencies for the individual types of electromagnetic radiation. It also provides information on the presence and strength of the individual types of bonds in the crystal and on the mobility of water and of the cations. It is thus an indispensable complement to X-ray (or neutron) diffraction in the study of crystalline substances.

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