

Infrared spectra of natural zeolites of the stilbite group

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The infrared absorption spectra of natural zeolites of the 7th structural group: heulandite, clinoptilolite, brewsterite, and stilbite were measured. The spectra were taken in the wavenumber region 200—4000 cm^{-1} by the KBr technique (1 : 40). The number and symmetry of individual vibrations were ascertained by theoretical factor-group analysis. The wavenumbers measured may be divided into four fundamental groups according to assignment to particular vibrations:

1. Stretching vibrations of the bonds inside the (Al, Si) O_4 tetrahedrons (wavenumbers 400—1100 cm^{-1});
2. Stretching vibrations of the OH groups of water molecules (wavenumbers 1590—1670 and 3400—3700 cm^{-1});
3. External vibrations between the (Al, Si) O_4 tetrahedrons (wavenumbers 300—500 and 1100—1250 cm^{-1});
4. Translation-rotation vibrations of the lattice and water molecules (wavenumbers 200—700 cm^{-1}).

The course of the spectra was subsequently confronted with structure and the character of bonds in these zeolites.

Были измерены инфракрасные абсорпционные спектры натуральных цеолитов 7-ой структурной группы: гейландита, клиноптилолита, брусстерита и стильбита. Спектры регистрировались в области волновых чисел 200—4000 см^{-1} с использованием техники КВг таблеток (1 : 40). Для определения числа и симметрии отдельных колебаний был проведен теоретический фактор-групповой анализ. Измеренные полосы в спектрах можно разделить на 4 основные группы по принадлежности к отдельным типам колебаний:

1. валентные колебания связей внутри (Al, Si) O_4 тетраэдров (область волновых чисел 400—1100 см^{-1});
2. валентные колебания ОН групп молекул воды (область волновых чисел 1590—1670 и 3400—3700 см^{-1});
3. внешние колебания между (Al, Si) O_4 тетраэдрами (область волновых

чисел 300—500 и 1100—1250 cm^{-1}); 4. поступательно-вращательные колебания ячейки и молекул воды (область волновых чисел 200—700 cm^{-1}).

Характер спектров сравнивался со структурой и характером связи этих цеолитов.

It is characteristic of the 7th structural group of zeolites [1] that their aluminosilicate framework consists of secondary building units 4—4—1, *i.e.* $(\text{Al}, \text{Si})_{10}\text{O}_{20}$. The minerals stilbite, heulandite, brewsterite, clinoptilolite, and stellerite belong to this group. Clinoptilolite is isostructural with heulandite and stellerite with stilbite, but the chemical composition and the Si/Al ratio are somewhat different. All minerals of this group exhibit laminated structure consisting of four- and five-membered rings TO_4 ($T = \text{Al}, \text{Si}$). Among these layers, there are channels where the cations and water molecules are located. Only the structures of stilbite and heulandite have been exactly described. The majority of these zeolites is temperature instable (a deformation of structure takes place with increasing temperature). Owing to this laminated structure, the zeolites of this group are called plastic zeolites. The basic physical parameters and theoretical chemical composition of these zeolites are given in Table 1.

Results

The polycrystalline samples of zeolites of the 7th group were subjected to measurements on a double-beam infrared spectrometer Perkin—Elmer, type 325, equipped with a grating monochromator by using the KBr technique (1 : 40). The absorption spectra were taken in the wavenumber range 200—4000 cm^{-1} at laboratory temperature. The authors did not succeed in getting from accessible sources the mineral stellerite belonging to this group.

The absorption spectra are shown in Figs. 1—4. The assignment of individual bands to certain vibrations (Table 2) was performed on the basis of literature data valid for analogous substances [2—5]. The number and symmetry of particular vibrations were ascertained by the factor-group analysis [6] the results of which are presented in Table 3.

Discussion

Except stilbite, all measured zeolites of this group give rise to broader bands in the wavenumber region 3400—3260 cm^{-1} which correspond to symmetric and asymmetric stretching vibration of the OH groups. The shift in wavenumbers with respect to equal vibration found for water vapour (3750 cm^{-1}) gives evidence of the presence of hydrogen bonds in the complex water—framework oxygen—cation. Owing to the effect of symmetry, it is possible to distinguish between asymmetric and symmetric stretching vibrations of the OH groups of stilbite with

Table 1
Physical and chemical properties of zeolites of the stilbite group

Mineral	Space group	Density	Hardness (Mohs)	Structural unit	Theoretical chemical composition, weight %					
					Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	H ₂ O	
Stilbite	<i>C2/m</i>	2.16	3.5—4	Na ₂ Ca ₄ [(AlO ₄) ₁₀ (SiO ₂) ₂₆]·28H ₂ O	2.16	7.84	17.82	54.58	17.60	
Heulandite	<i>C_m</i>	2.19	3.5—4	Ca ₄ [(AlO ₂) ₈ (SiO ₂) ₂₈]·24H ₂ O	—	8.17	14.85	61.26	15.72	
Clinoptilolite	<i>I2/m</i>	2.16	?	Na ₆ [(AlO ₂) ₆ (SiO ₂) ₃₀]·24H ₂ O	6.82	—	11.22	66.12	15.84	
Brewsterite	<i>P2₁/m</i>	2.45	5	(Sr, Ba, Ca) ₂ [(AlO ₂) ₄ (SiO ₂) ₁₂]·10H ₂ O	—	MeO*	15.88	15.53	54.89	13.70
Stellerite	—	—	—	—	—	—	—	—	—	

* Calculated to mean molecular weight MeO = 104.36.

Table 2

Infrared absorption bands of zeolite of the stilbite group

Mineral (locality)	OH stretch. sym. and asym.	Overtone in plane bending H—O—H	Bending H—O—H	External TO ₄	Asym. stretching T—O	Sym. stretching T—O	H ₂ O libration	Doublet rings	Bending O—T—O	Transla- tional H ₂ O	Optical translational mode of lattice (LO ⁺ TO)*
Stilbite ¹	3380 m 3440 vs	2920 w	1630 m	1190 vs 1130—1170 vs	1080 vs 990 s	750 s	660 w 620 s 600 m 480 vw 450 vw	520 split 530 m	440 vw	340 m	250 m
Heulandite ²	3620—3500 m	2920 vw	1640 m	—	1070—1000 vs	790 vw 720 vs	590 vw	—	460—440 w	—	230 w
Brewsterite ³	3580—3400 s	2920 vw	1640 m	—	1020—1000 vs	790 vw	530 vw	—	460—440 w	—	230 m
Clinopti- lolite ⁴	3420—3640 s	2920 vw	1630 m	1210 vw 1390 vw	1040—1070 m	800 m	610 w 470 s	520 vw	400 vw	350 vw	230 vs

vs — very strong, s — strong, m — medium, w — weak, vw — very weak.

* Interactions with vibrations of the KBr matrix; T = Al, Si.

1 — Fassa, Italy; 2 — mountains Bhor-Ghet, India; 3 — Strontian, Scotland; 4 — Nižný Hrabovec.

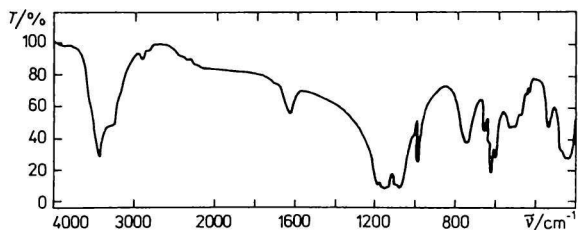


Fig. 1. Infrared spectrum of stilbite (Fassa — Italy).

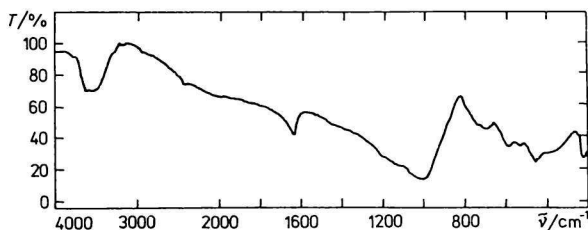


Fig. 2. Infrared spectrum of heulandite (mountains Bhor Ghet — India).

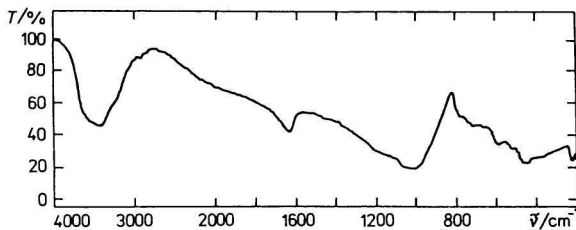


Fig. 3. Infrared spectrum of brewsterite (Strontian — Scotland).

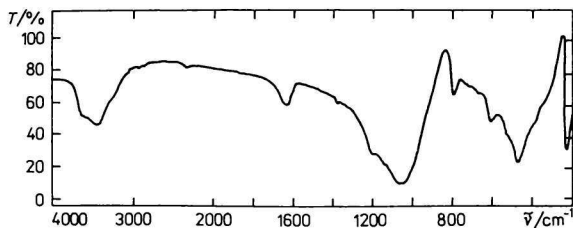


Fig. 4. Infrared spectrum of clinoptilolite (Nižný Hrabovec).

Table 3

Factor-group analysis of the measured zeolites

E	Identity
σ_h	Horizontal symmetry plane
T_x, T_y, T_z	Translation along axes x, y, z
R_x, R_y, R_z	Rotation about axes x, y, z
$\alpha_x, \alpha_y, \alpha_z$	Polarizability tensors in the sense of axes x, y, z
i.r.	Active vibration in infrared spectrum
R	Active vibration in Raman spectrum
$A, A_g, A_u, B_g, B_u, F_2$	Denotation of uncontrollable representations of symmetry elements
$\nu_1, \nu_2, \nu_3, \nu_4$	Individual vibrations
TO_4	Tetrahedrons of the oxygen—silicon and oxygen—aluminium point group of symmetry (isomorphous to crystallographic space group)
T_d	Tetragonal
C_{2v}	Orthorhombic
D_2	Orthorhombic
C_s	Monoclinic
C_{2h}	Monoclinic
C_2	Monoclinic
C_1	Monoclinic
Θ	Angle of rotation
N	Number of atoms
$N_{(a)}$	Number of atom groups
$N_{(a-m)}$	Number of polyatomic groups
i	Inversion
x^t	Number of all vibrations
x^i	Number of internal vibrations
x^{tr}	Number of translational vibrations
x^r	Number of rotational vibrations
x^a	Number of acoustic vibrations

the wavenumbers 3440 and 3380 cm^{-1} which exhibit a great shift toward lower wavenumbers. This fact indicates rather strong hydrogen bonds with oxygen atoms of the Si—O—Al bridges. With all investigated minerals, the bands of the wavenumber 2920 cm^{-1} belonging to overtone harmonic vibration of in plane bending vibration of H—O—H were found. The medium intensity bands of the bending H—O—H vibration occur in the wavenumber region $1630\text{—}1640\text{ cm}^{-1}$. The very strong and broad bands with fine structure or splits of the asymmetric stretching vibration of the T—O bonds appear in the wavenumber region $990\text{—}1190\text{ cm}^{-1}$. Owing to similar force constants of the Al—O and Si—O bonds, the vibrations of these bonds are not distinguishable. As this vibration shifts toward lower wavenumbers [2] with increasing content of the Al atoms in the structure, we

may approximately determine the ratio of atoms Si/Al according to the published empirical relationships [2]. The shifts in these wavenumbers are different for the measured zeolites, which demonstrates different Si/Al ratios in these minerals. Varying broadness of these bands with structure and splits manifest inhomogeneity of the force fields. The weak bands of symmetric stretching vibration of the T—O bonds occur in the wavenumber region 750—790 cm^{-1} .

The weak bands of bending vibrations of O—T—O are in the wavenumber region 440—480 cm^{-1} . With heulandite and brewsterite, there are only simple weak bands of water libration at 590 cm^{-1} . It is a consequence resulting from the effect of high symmetry fields on water molecules owing to which there is only one degree of freedom of rotational motion along axis *c* of the H—O—H molecules. As to stilbite, seven bands of different intensity with splits occur in the wavenumber range 450—660 cm^{-1} . It is evident that the bands of water libration and the bands of external vibrations of the conjoint TO_4 rings overlap. That enables us also to assume the presence of two kinds of hydrogen bonds and two degrees of rotational freedom of water molecules along the axis *a* and the axis *c* of molecule. For clinoptilolite, two bands of this libration which can indicate two degrees of rotational motion of water molecules have been found. Only for stilbite and clinoptilolite, the bands of translational modes of water molecules in resonance with crystal lattice of minerals have been found at the wavenumber of 340 cm^{-1} . The bands of varying intensities of the translational mode of lattice in interactions with vibrations of the KBr matrix occur in the wavenumber region 230—240 cm^{-1} .

Conclusion

For zeolites of the 7th structural group, a low symmetry of crystal lattice (they are monoclinic) has been found [2]. The layers in all minerals formed by secondary building units $\text{T}_{10}\text{O}_{20}$ of the (4—4—1) structure are oriented in a direction parallel to the crystallographic [010] direction. Between individual layers there are channels consisting of eight-membered rings of oxygen atoms where the cations and water molecules are localized [2].

The wavenumbers of particular vibrations found experimentally may be divided into four main groups:

1. Stretching vibrations of water molecules (wavenumbers 1600—1650 and 3400—3650 cm^{-1});
2. Stretching vibrations of the bonds inside the TO_4 (T = Al, Si) tetrahedrons (wavenumbers 400—1100 cm^{-1});
3. External vibrations of the TO_4 tetrahedrons (wavenumbers 300—500 and 1100—1250 cm^{-1});

Table 4
Irreducible representations

1. Stilbite						
Factor group	Symmetry elements					
C_{2h}	F	C_2	σ_h	i		
A_g	1	1	1	1		$R_x, \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
A_u	1	1	-1	-1		T_z
B_g	1	-1	-1	1		$R_x, R_y, \alpha_{yz}, \alpha_{zx}$
B_u	1	-1	1	1		T_x, T_y
	0	180	0	180		
$\text{COS } \Theta$	1	-1	1	-1		
$1 \pm 2\text{COS } \Theta$	3	-1	1	-3		
N	200	0	0	0		
$N_{(a)}$	21	0	0	0		
$N_{(a)-1}$	20	-1	-1	-1		
$N_{(a-m)}$	12	0	0	0		
x^t	600	0	0	0		
x^j	504	0	0	0		
x^{ir}	60	1	-1	3		
x^r	36	0	0	0		
x^s	3	-1	1	-3		
C_{2h}	x^t	x^j	x^{ir}	x^r	x^s	
A_g	150	126	16	9	0	R
A_u	150	126	14	9	1	i.r.
B_g	150	126	16	9	0	R
B_u	150	126	14	9	2	i.r.

Table 4 (Continued)

2. Heulandite						
Factor group		Symmetry elements				
C_2	E	σ_h				
A'	1	1	$T_x, T_y, R_z, \alpha_{xx}, \alpha_{yy}, \alpha_{xy}, \alpha_{zz}$			
A''	1	-1	$T_x, R_x, R_y, \alpha_{yz}, \alpha_{zx}$			
	0	0				
$\text{COS } \Theta$	1	1				
$1 \pm 2\text{COS } \Theta$	3	-1				
N	184	0				
$N_{(0)}$	16	0				
$N_{(0)-1}$	17	-1				
$N_{(a-m)}$	12					
x^t	552	0				
x^i	468	0				
x^v	45	-1				
x^r	36	0				
x^a	3	1				
C_2	x^t	x^i	x^v	x^r	x^a	
A'	276	234	23	18	2	i.r., R
A''	276	234	22	18	1	i.r., R

Table 4 (Continued)

3. Brewsterite						
Factor group	Symmetry elements					
C_{2h}	E	C_2	σ_h	i		
A_g	1	1	1	1		$R_z, \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
A_u	1	1	-1	-1		T_z
B_g	1	-1	-1	1		R_x, R_y
B_u	1	-1	1	-1		T_x, T_y
	0	180	0	180		
$\cos \theta$	1	-1	1	-1		
$1 \pm 2\cos \theta$	3	-1	-1	3		
N	64	0	0	0		
$N_{(s)}$	4	0	0	0		
$N_{(s)-1}$	3	-1	-1	-1		
$N_{(s-m)}$	3	0	0	0		
x^i	192	0	0	0		
x^i	188	0	0	0		
x^{ir}	9	1	-1	3		
x^r	9	0	0	0		
x^s	3	-1	1	-3		
C_{2h}	x^i	x^i	x^{ir}	x^r	x^s	
A_g	48	46	3	2	0	R
A_u	48	46	2	2	1	i.r.
B_g	48	46	3	2	0	R
B_u	48	46	1	3	2	i.r.

Table 4 (Continued)

4. Clinoptilolite

Factor group	Symmetry elements					
C_{2h}	E	C_2	σ_h	i		
A_g	1	1	1	1		$R_z, \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
A_u	1	1	-1	-1		T_z
B_g	1	-1	-1	1		$R_x, R_y, \alpha_{yz}, \alpha_{zx}$
B_u	1	-1	1	-1		T_x, T_y
	0	180	0	180		
$\text{COS } \theta$	1	-1	1	-1		
$1 \pm 2\text{COS } \theta$	3	-1	1	-3		
N	186	0	0	0		
$N_{(g)}$	24	0	0	0		
$N_{(g)-1}$	23	-1	-1	-1		
$N_{(g-m)}$	18	0	0	0		
x^t	558	0	0	0		
x^i	432	0	0	0		
x^{iv}	69	1	-1	3		
x^r	54	0	0	0		
x^s	3	-1	1	-3		
C_{2h}	x^t	x^i	x^{iv}	x^r	x^s	
A_g	137	108	18	14	0	R
A_u	137	108	17	13	1	i.r.
B_g	137	108	18	13	0	R
B_u	137	108	16	14	2	i.r.

Table 5

Correlation diagram between symmetry elements of individual groups

1. Stilbite		
Point group	Site group	Factor group
T_d (TO_4)	C_1	C_{2h}
$v_1(A_1)$ $v_2(E)$ $v_3, v_4(F_2)$	A	v_1 v_2 v_3, v_4
		$14(A_g + B_g + A_u + B_u)$ $28(A_g + B_g + A_u + B_u)$ $42(A_g + B_g + A_u + B_u)$
C_{2v} (H_2O)	C_1	C_{2h}
$v_1, v_3(A_1)$ $v_2(B_2)$	A	v_1 v_2 v_3
		$14(A_g + B_g + A_u + B_u)$ $14(A_g + B_g + A_u + B_u)$ $14(A_g + B_g + A_u + B_u)$

Table 5 (Continued)

2. Heulandite		
Point group	Site group	Factor group
T_d (TO_4)	C_1	C_s
$v_1(A_1)$ $v_2(E)$ $v_3, v_4(F_2)$	A	v_1 v_2 v_3 v_4
		$39(A')$ $39(A' + A'')$ $39(2A' + A'')$ $39(2A' + A'')$
C_{2v} (H_2O)	C_1	C_s
$v_1, v_3(A_1)$ $v_2(B_2)$	A	v_1 v_2 v_3
		$39(A')$ $39(A')$ $39(A')$

Table 5 (Continued)

3. Brewsterite				
Point group	Site group		Factor group	
T_d (TO ₄)	C_3		C_{2h}	
			R	i.r.
$\nu_1(A_1)$ —————	A' —————	ν_1 —————	A_g	B_u
$\nu_2(E)$ —————	$A' + A''$ —————	ν_2 —————	$A_g + B_g$	$A_u + B_u$
$\nu_3(F_2)$ —————	$2A' + A''$ —————	ν_3 —————	$2A_g + B_g$	$A_u + B_u$
$\nu_4(F_2)$ —————	$2A' + A''$ —————	ν_4 —————	$2A_g + B_g$	$A_u + B_u$
C_{2v} (H ₂ O)	C_2		C_{2h}	
			R	i.r.
$\nu_1(A_1)$ —————	A' —————	ν_1 —————	A_g	B_u
$\nu_3(A_1)$ —————	A' —————	ν_2 —————	A_g	B_u
$\nu_2(B_2)$ —————	A'' —————	ν_3 —————	B_g	A_u

Table 5 (Continued)

4. Clinoptilolite		
Point group	Site group	Factor group
T_d (TO_4)	C_1	C_{2h}
$v_1(A_1)$	A	v_1 9($A_g + B_g + A_u + B_u$)
$v_2(E)$		v_2 18($A_g + B_g + A_u + B_u$)
$v_3, v_4(F_2)$		v_3 27($A_g + B_g + A_u + B_u$)
		v_4 27($A_g + B_g + A_u + B_u$)
C_{2v} (H_2O)	C_1	C_{2h}
$v_1, v_3(A_1)$	A	v_1 9($A_g + B_g + A_u + B_u$)
$v_2(B_2)$		v_2 9($A_g + B_g + A_u + B_u$)
		v_3 9($A_g + B_g + A_u + B_u$)

4. Translation-rotation vibrations of the lattice and water molecules (wavenumbers 200—320 and 440—680 cm^{-1}).

In conclusion, it may be stated that the results obtained by experiments are in good agreement with the theory and structure of these zeolites and complete the knowledge obtained by other methods (Tables 4 and 5).

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