

Vibrational spectra in far infrared region of natural zeolites of the natrolite group

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Received 28 December 1981

The spectra of the cation—oxygen vibrations of selected types of zeolites of the natrolite group (natrolite, mesolite, and scolecite) were measured in far infrared region in the range of wavenumbers 50—400 cm^{-1} . The samples were prepared at $\Theta/^\circ\text{C}$: 23, 100, 200, 300, and 400 and the spectra were taken under normal laboratory conditions. The wavenumbers were assigned to the Na...O, K...O, and Ca...O vibrations in individual investigated minerals on the basis of the change in content of the Na^+ , K^+ , and Ca^{2+} cations and on the basis of literature data.

The wavenumbers obtained from spectra are approximately governed by the expression $\nu = C/m^{1/2} R^{3/2}$ which was taken from literature.

В диапазоне частот 50—400 cm^{-1} (дальняя инфракрасная область) были сняты спектры колебаний связи катион—кислород избранных типов цеолитов группы натролита: натролита, мезолита и сколецита. Образцы были приготовлены при температурах $\Theta/^\circ\text{C}$: 23, 100, 200, 300 и 400, а спектры снимались при нормальных лабораторных условиях. Соответствие между наблюдаемой частотой колебания и типом связи Na...O, K...O, Ca...O было установлено на основании наблюдения изменений содержания катионов Na^+ , K^+ , Ca^{2+} у отдельных изучаемых минералов и на основе литературных данных.

Найденные по спектрам частоты приблизительно соответствуют формуле $\nu = C/m^{1/2} R^{3/2}$, взятной из литературы.

According to *Breck* [1], natural zeolites such as natrolite



mesolite



and scolecite



belong into the fifth structural group of zeolites. The minerals of this group exhibit characteristic fibrous habit of their crystals. This morphology is due to the fact that the (Al, Si)O₄ tetrahedrons are connected in chains according to the crystallographic axis *c* and form secondary building units of the 4—1 structure [1]. A system of polyhedral holes arises among these chains where the cations and water molecules are localized. The cations provide ion—dipole interactions for oxygen atoms in the molecules of water and framework of the structure. In all investigated minerals, sodium and potassium are coordinated with six oxygen atoms in the configuration of distorted octahedron while calcium in natrolite is coordinated with four oxygen atoms and in other minerals with seven oxygen atoms in the configuration of distorted pentagonal bipyramid [2—7]. Other cations occur in negligible amount in the structure and do not give any distinguishable spectral bands. Recently, the infrared spectroscopy proved to be a convenient method for studying the interionic vibrations [8, 9]. For instance, *Brodskii et al.* [8] measured the far infrared spectra of the interionic vibrations in synthetic zeolites of the series X and Y. *Exharthos* [9] measured these spectra for ionic glasses. Both authors have deduced that the wavenumbers of the cation—oxygen vibrations are approximately proportional to the expression $C/m^{1/2}R^{3/2}$ where *m* is the mass of cation, *R* is its radius, and *C* is a constant of proportionality. Simultaneously, *Exharthos* calculated the force constants for the Na...O, K...O, and Ca...O vibrations as well as the theoretical wavenumbers for the octahedral field *T_{1g}*. The values of these parameters are as follows: Na...O, $F=177 \times 10^{-6} \text{ Nm}^{-1}$, $\nu=212 \text{ cm}^{-1}$; K...O, $F=112 \times 10^{-6} \text{ Nm}^{-1}$, $\nu=147 \text{ cm}^{-1}$; Ca...O, $F=363 \times 10^{-6} \text{ Nm}^{-1}$, $\nu=263 \text{ cm}^{-1}$. Moreover, both authors investigated the change in wavenumbers in the course of ion-exchange reactions and diffusion processes. These data may give information about the use of zeolites as ion-exchangers and molecular sieves in technical practice.

Experimental

The samples of natural zeolites (natrolite, mesolite, and scolecite) used for measurement at laboratory temperature were prepared in the form of aqueous emulsion of polycrystalline material and put on a plate of synthetic silicon. For measurements at higher temperature, the samples were isothermally heated in a special vacuum apparatus [10] and subsequently sealed in polyethylene foils. The spectra were taken under laboratory conditions. The measurements were carried out *in vacuo* with a FIR interferometer HITACHI FIS-1. The investigated range of wavenumbers was 50—400 cm⁻¹. The spectral measurements were processed with a computer IBM 370. The accuracy of reading was $\pm 2 \text{ cm}^{-1}$.

Results and discussion

The observed wavenumbers as well as their assignment to individual vibrations are presented in Table 1. The spectra obtained by means of a coordinate recorder IBM are shown in Figs. 1—4.

Table 1

Wavenumbers observed and their assignment from the far infrared spectra of natrolite, mesolite, and scolecite and their temperature dependence (23—400°C)

Zeolite	<i>t</i> /°C	$\tilde{\nu}$ /cm ⁻¹					
		T...T	Ca...O	Na...O	K...O	T...T	
Natrolite	23	360 m	264 w	190 s	110 w	88 w	65 w
	100	360 m	265 vw	192 s	110 w	89 w	65 vw
	200	363 m	inf.	199 s	109 w	90 vw	66 vw
	300	365 m	—	199 s	108 w	91 vw	69 vw
	400	365 m	—	201 s	inf.	inf.	inf.
Mesolite	23	362 m	260 s	190 s	110 vw	87 w	68 w
	100	363 m	263 s	192 s	110 vw	88 w	68 w
	200	363 m	265 s	196 s	—	88 vw	69 vw
	300	365 m	265 m	198 s	—	inf.	inf.
	400	368 m	268 m	200 s	—	—	—
Scolecite	23	364 m	275 s	—	—	90 w	62 w
	100	365 m	276 s	—	—	92 vw	63 vw
	200	368 m	278 s	—	—	94 vw	64 vw
	300	inf.	279 m	—	—	—	—
	400	—	inf.	—	—	—	—

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

The individual wavenumbers were assigned to the cation—oxygen vibrations according to literature data [8, 9] as well as on the basis of the presence of the cations in individual minerals to which the individual bands in the far infrared spectra corresponded. The medium bands in the region 360—368 cm⁻¹ which were present in the spectra of all investigated minerals may be assigned to the translational vibration of the structural framework [8]. The intensive bands observed in the spectra of mesolite and scolecite as well as the weak bands in the spectrum of natrolite which appear in the wavenumber range 260—279 cm⁻¹ may be assigned to vibration of the Ca...O bond [8, 9]. These wavenumbers approximately correspond to the theoretically calculated ones (263 cm⁻¹) [9]. The weak bands at the wavenumbers of 110 cm⁻¹ may be attributed to the K...O vibration [8, 9], the theoretical value being 147 cm⁻¹ [9]. The intensive band in the

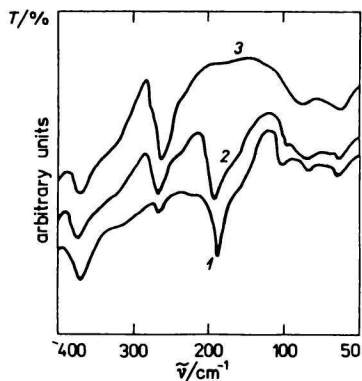


Fig. 1. Far infrared spectra of zeolites of the natrolite group at laboratory temperature.

1. Natrolite; 2. mesolite; 3. scolecite.
Range of wavenumbers 50–400 cm^{-1} .

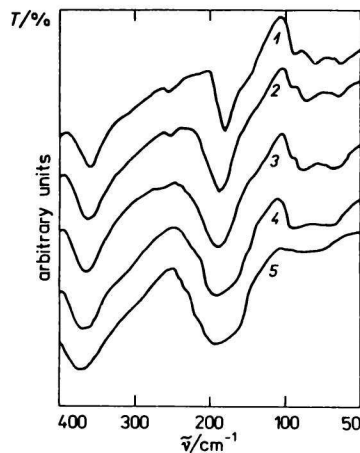


Fig. 2. Temperature dependence of far infrared spectra of natrolite in the wavenumber range 50–400 cm^{-1} .

1. 23°C; 2. 100°C; 3. 200°C; 4. 300°C;
5. 400°C.

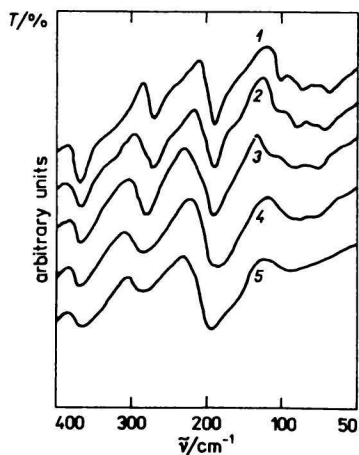


Fig. 3. Temperature dependence of far infrared spectra of mesolite in the wavenumber range 50–400 cm^{-1} .

1. 23°C; 2. 100°C; 3. 200°C; 4. 300°C;
5. 400°C.

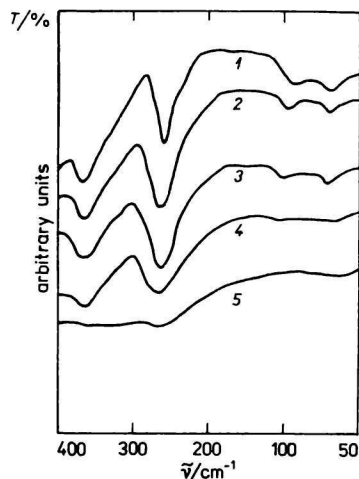


Fig. 4. Temperature dependence of far infrared spectra of scolecite in the wavenumber range 50–400 cm^{-1} .

1. 23°C; 2. 100°C; 3. 200°C; 4. 300°C;
5. 400°C.

wavenumber range $190\text{--}201\text{ cm}^{-1}$ appearing in the spectra of natrolite and mesolite corresponds to vibration of the Na...O bond [8, 9]. The theoretical value of wavenumber of this vibration is 212 cm^{-1} [9]. The weak bands in the range of wavenumbers $88\text{--}94\text{ cm}^{-1}$ and $62\text{--}69\text{ cm}^{-1}$ which occur in the spectra of all investigated zeolites may be assigned to the vibrations in the cation—H₂O and cation—OH—framework complex or to the optical translational vibration of framework. As for temperature dependence of the far infrared spectra, we could observe a shift in all vibrations to higher wavenumbers, extension of bands and disappearance of some vibrations at temperatures of $300\text{--}400^\circ\text{C}$.

The shift in the cation—oxygen vibrations at increased temperatures results from the fact that the cations approach owing to diffusion processes the walls of polyhedral holes where they can more intensely interreact with the oxygen atoms in framework or structural hydroxyls. The similarity between wavenumbers of vibrations of equal cations present in different zeolites gives evidence that similar force fields with similar symmetry (T_{1u} or O_h) exert influence on these cations. Because of the shift in wavenumbers of interionic vibrations at increased temperatures, we may assume equal activation energies of the diffusion motion of cations [9].

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Translated by R. Domanský