

INFRARED SPECTRA OF THE NATURAL ZEOLITE HEULANDITE

František PECHAR

*Institute of Geology and Geotechnics,
Czechoslovak Academy of Sciences, 182 09 Prague 8*

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The mid-infrared ($4\,000\text{--}200\text{ cm}^{-1}$) absorption spectra, far infrared ($400\text{--}40\text{ cm}^{-1}$) absorption spectra, infrared ($1\,400\text{--}200\text{ cm}^{-1}$) reflection spectra, and Raman spectra ($3\,600\text{--}50\text{ cm}^{-1}$) were measured at room temperature for polycrystalline heulandite, a natural zeolite from Poonah, India.

Three optical methods can be used for obtaining the vibrational spectra of crystals: absorption of infrared radiation, reflection of infrared radiation, and Raman scattering of visible radiation. These methods complement each other experimentally as well as from the point of view of the operating selection rules. The band positions and intensities for the various vibrational transitions can serve as the starting data for the calculation of the dispersion of the optical constants of minerals (complex refractive index, complex dielectric permittivity, absorbance, extinction, etc.), bond force constants, bond energies, and vibrational mean square amplitudes. In this respect, vibrational spectra are complementary to the diffraction methods of investigation of crystalline substances. The theory of the spectroscopic methods can be found elsewhere¹⁻³.

Heulandite, whose crystals belong to the *Cm* monoclinic space group, has been classed by Bröck⁴ in zeolite structure class 7, characterized by secondary building units of 4-4-1 structure, *i.e.*, the units contain two four-membered rings of $(\text{Al}, \text{Si})\text{O}_4$ tetrahedra and a five membered ring which are mutually linked to form a complex unit. The units are further linked into a threedimensional network of the crystal in which cavities and channels occur. The cavities contain Ca^{2+} cations and water molecules; each calcium cation is surrounded by three oxygen atoms from the framework and coordinates five molecules of water.

EXPERIMENTAL

The natural zeolite heulandite (locality of Poonah, India) had a crystallochemical formula $(\text{Na}_{1.14}\text{K}_{0.06}\text{Ca}_{3.84})[(\text{Al}_{8.51}\text{Fe}_{0.06}\text{Si}_{27.22})\text{O}_{72}]\cdot 28.64\text{ H}_2\text{O}$ as obtained from the chemical analysis (the chemical composition was 57.43% SiO_2 , 15.24% Al_2O_3 , 1.24% Na_2O , 0.10% K_2O , 7.58% CaO , 0.09% MgO , traces of MnO , 0.16% Fe_2O_3 , and 18.10% H_2O — total of 99.94%). The $\text{Si}/(\text{Si} + \text{Al})$ ratio was 0.769.

The mid-infrared spectra of polycrystalline heulandite were scanned on a Perkin-Elmer 325 grating spectrophotometer. The transmission and reflection spectra were obtained using a powder sample in KBr disks and an optically polished polycrystalline sample, respectively. The sample reflectance is related to that of an aluminium mirror. The far-infrared spectrum was run for

a powder sample dispersed in a polyethylene foil at 200°C; the measurements were performed at a reduced pressure using a rotary oil pump. A Beckman FS-720 interferometer was used and the Fourier transform was performed on an IBM 370 computer.

The nonpolarized Raman spectrum of heulandite crystals fixed to a quartz rod was obtained with a Spex 14018 instrument equipped with an Ar laser working at 514.5 nm. The accuracy of the wavenumber reading was ± 2 to ± 5 cm^{-1} .

RESULTS AND DISCUSSION

The spectra obtained are reproduced in Figs 1–4. The band assignment was performed based on published data for related substances^{4–6}; the results are presented in Table I. All the spectra exhibit well-resolved bands of the various vibrations superimposed on a considerably high background. The spectra can be compared in three groups with respect to the wavenumber ranges covered:

3 700–1 400 cm^{-1} – mid-infrared and Raman spectra;

1 400– 200 cm^{-1} – mid-infrared and partly far-infrared spectra, reflection spectra;

200– 40 cm^{-1} – Raman and far-infrared spectra.

Our infrared spectrum of natural heulandite differs substantially from that of this mineral published by Breck⁴, both in the overall spectral patterns and the band positions. For example, Breck reports three OH stretching vibration bands at 3 600, 3 500, and 3 400 cm^{-1} , whereas our spectrum displays a single broad band over the 3 650–3 450 cm^{-1} range. The band at 1 600 cm^{-1} , which can be attributed to H–O–H bending, is absent from the spectrum⁴. The spectrum by Breck exhibits five bands of M–O stretching vibrations at 1 200, 1 050, 800, 720, and 660 cm^{-1} , whereas our spectrum shows a weak band at 1 200 cm^{-1} , a broad strong band over the 1 060–980 cm^{-1} range, and a weak band at 710 cm^{-1} . The bands due to the H₂O

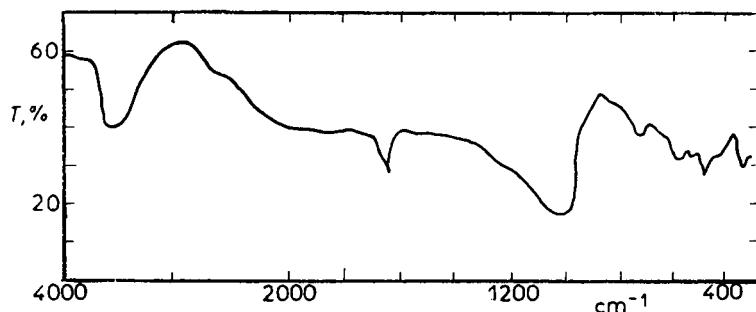


FIG. 1

Infrared absorption spectrum of heulandite (powder sample in a KBr disk)

librations are found at 600 and 510 cm^{-1} in the former and at 605 and 520 cm^{-1} in the latter spectra, the bands of the bending vibrations lie at 440 and 460 cm^{-1} in the two spectra, respectively.

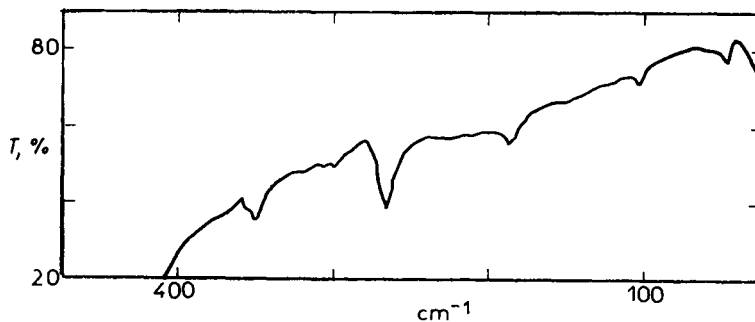


FIG. 2

Far-infrared absorption spectrum of heulandite (powder sample in a polyethylene foil)

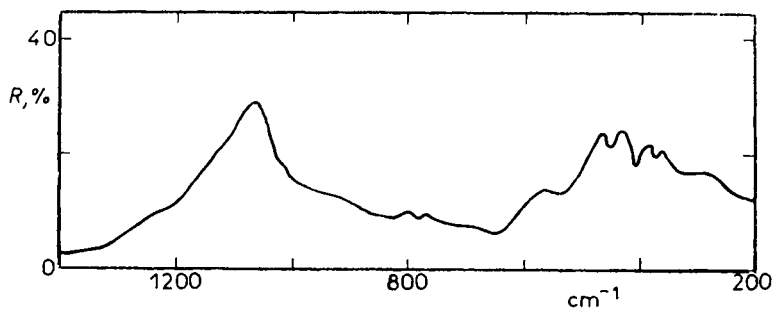


FIG. 3

Infrared reflection spectrum of heulandite (optically polished polycrystalline sample)

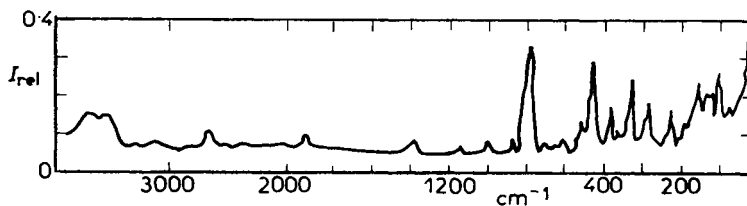


FIG. 4

Nonpolarized Raman spectrum of heulandite (polycrystalline sample fixed to a quartz rod)

This implies that the two zeolites probably differ in their chemical composition, which brings about local differences in their structure. These differences also concern the Si(Al)—O bond length and bond strength. The changes in the cation content in turn affect the local force fields and symmetry of the structure fragments. All these effects then appear in the overall spectral patterns as well as the band positions and intensities. In this respect the vibrational spectra are a convenient tool for the investigation of the structure arrangement in these complex minerals, and they also can serve for identification purposes, because no two zeolite spectra^{4,5} are identical with each other.

The far infrared absorption spectra, infrared reflection spectra, or Raman spectra of this mineral have not been so far published (to the author's knowledge), and the assignment of the bands observed was performed based on that reported for allied substances⁶⁻¹¹. Our Raman spectrum of heulandite is completely different from the

TABLE I

Vibrational spectra of heulandite (Poonah, India). Band positions in cm^{-1} , relative intensities: vs very strong, s strong, m medium, w weak, vw very weak

| Vibration | Spectrum | | | |
|---|-------------------------|---------------------------|---------------------------|----------------------|
| | infrared ^{4,5} | far infrared ⁶ | reflection ^{4,5} | Raman ^{4,5} |
| O—H stretching | 3 650—3 450 vs | — | — | 3 650 w |
| | | | | 3 500 w |
| H—O—H bending | 1 650 m | — | — | 1 595 w |
| M—O stretching | 1 200—980 vs | — | 1 080 vs | 1 200—1 040 w |
| | | | 795 vs | 980 vs |
| | | | 780 vw | 950 w |
| | | | | 870 w |
| | | | | 810 w |
| | | | | 680 w |
| | | | | 630 vs |
| H ₂ O librations | 605 w | — | 580—630 m | 590 s |
| | | | | 580 w |
| | | | | 530 w |
| | | | | 430 s |
| Bending O—M—O | 460 m | — | 460 s | |
| | | | 430 s | |
| Pore opening | — | 345 w | 395 w | 490 m |
| | | | 370 w | |
| Ca—O stretching | — | 260 m | — | 250 m |
| Lattice or Ca—H ₂ O complex vibrations | 220 m | 190 w | 300—280 w | 195 w |
| | | 105 vw | | 155 m |
| | | 49 w | | 95 vw |

published spectra¹⁰ of similar substances. Only the reflection spectra resemble those of silicates and aluminosilicates^{8,9,11}, the band positions and structure, however, are again different.

It can be concluded that none of the vibrational spectra obtained in this work is identical with any published spectrum. The spectra thus can be employed for the identification of the minerals and for the study of their structure arrangement. The mid-infrared spectra provide expeditious information on the vibrations of the "zeolite" water and their symmetry. The length of the OH...O bonds available for hydrogen bond formation⁷ can be determined and the hydrogen bond type and strength assessed based on the shift of the bands of the water OH bonds with respect to the corresponding bands for water vapours, using published graphs³. Similarly, the fraction of aluminium in the (Al, Si)O₄ tetrahedra can be estimated from the shift of the bands of the (Al, Si)—O bond stretching with respect to those of the pure Si—O bond, employing the graph published by Breck⁴. Information about vibrations of the cation–oxygen bonds and the cation–water complex and their energies can be derived from the far-infrared and Raman spectra. The reflection spectra are highly sensitive to vibrations of the structure framework, and the dispersion curves of the optical constants over the wavenumber region measured can be calculated from them by using the Kramers–Kronig relations. So, vibrational spectra complement conveniently the diffraction methods in the study of the crystallo-chemical parameters of minerals and other solids.

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REFERENCES

1. Poulet H., Mathieu J. P.: *Spectres de vibration et symétrie des cristaux*. Gordon et Breach, Paris 1973.
2. Ross S. D.: *Inorganic Infrared and Raman Spectra*. McGraw-Hill, London 1972.
3. Turell G.: *Infrared and Raman Spectra of Crystals*. Academic Press, London 1972.
4. Breck D. W.: *Zeolite Molecular Sieves, Structure, Chemistry, and Use*. Wiley, New York 1974.
5. Flaningen E. M., Khatami H., Szymanski H. A.: *Advan. Chem. Ser.* 101, 201 (1971).
6. Exharthos G. J., Miller J. P., Rise W. M.: *Chem. Phys.* 60, 4145 (1974).
7. Hamilton W. C., Ibers J. A.: *Hydrogen Bonding in Solids*. Benjamin, New York 1968.
8. Pechar F.: *Krist. Tech.* 20, 2, 239 (1985).
9. Vlasov A. G.: *Infrakrasnye Spektry Neorganicheskikh Stekol i Kristallov*. Khimiya, Leningrad 1972.
10. Pechar F.: *This Journal* 46, 3038 (1981).
11. Pechar F.: *N. Jb. Miner. Mh.* 8, 351 (1983).

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