

RAMAN SPECTROSCOPY OF ZEOLITES: CHARACTERIZATION OF NATURAL ZEOLITES WITH THE LASER RAMAN MICROPROBE

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Raman spectra were collected from 14 natural zeolites (Table 1) as part of an ongoing project to provide a basis for identification of zeolites and to accumulate data for theoretical interpretations. Spectral features observed for these zeolites occur primarily in the $<600\text{ cm}^{-1}$ structurally sensitive region of the spectrum, facilitating identification of these zeolites on a structural basis. Although apparent relationships between zeolite structure and Raman spectra have been noted for some zeolites in prior studies, to the authors' knowledge there has been no comprehensive evaluation of this relationship to date.

TABLE 1.--Names, average chemical compositions, symmetry, and catalog numbers of zeolite minerals surveyed in this study. Specimens belong to the Geological Sciences Museum at VPI&SU, and the Geology Department of Radford University.

Zeolite	Typical unit-cell formula	Crystal system	Catalog No.
Analcime	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96})\cdot 16\text{H}_2\text{O}$	cubic	B393
Phillipsite	$(\text{Na,K})_{10}(\text{Al}_{10}\text{Si}_{22}\text{O}_{62})\cdot 20\text{H}_2\text{O}$	orthorhombic	B216
Harmotome	$\text{Ba}_2(\text{Al}_4\text{Si}_{12}\text{O}_{32})\cdot 12\text{H}_2\text{O}$	orthorhombic	M1207
Chabazite	$(\text{Na}_2,\text{Ca})_6(\text{Al}_{12}\text{Si}_{24}\text{O}_{72})\cdot 40\text{H}_2\text{O}$	trigonal	B267
Gmelinite	$\text{Na}_8(\text{Al}_8\text{Si}_{16}\text{O}_{48})\cdot 24\text{H}_2\text{O}$	hexagonal	64
Faujasite	$\text{Na}_{58}(\text{Al}_{58}\text{Si}_{134}\text{O}_{384})\cdot 240\text{H}_2\text{O}$	cubic	1646
Heulandite	$\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 24\text{H}_2\text{O}$	monoclinic	1607
Stilbite	$\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 28\text{H}_2\text{O}$	monoclinic	150*
Natrolite	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{24}\text{O}_{80})\cdot 16\text{H}_2\text{O}$	orthorhombic	B208
Mesolite	$\text{Na}_{16}\text{Ca}_{16}(\text{Al}_{48}\text{Si}_{72}\text{O}_{240})\cdot 64\text{H}_2\text{O}$	orthorhombic	D13
Scolecite	$\text{Ca}_8(\text{Al}_{16}\text{Si}_{24}\text{O}_{80})\cdot 24\text{H}_2\text{O}$	monoclinic	1619
Thomsonite	$\text{Na}_4\text{Ca}_8(\text{Al}_{20}\text{Si}_{20}\text{O}_{80})\cdot 24\text{H}_2\text{O}$	orthorhombic	1609
Mordenite	$\text{Na}_8(\text{Al}_8\text{Si}_{40}\text{O}_{96})\cdot 24\text{H}_2\text{O}$	orthorhombic	1614
Epistilbite	$\text{Ca}_3(\text{Al}_6\text{Si}_{18}\text{O}_{48})\cdot 18\text{H}_2\text{O}$	monoclinic	70

Experimental Methods

Raman spectra are collected with an Instruments SA Ramanor U-1000 laser Raman spectrom-

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ter coupled with an Olympus BH-2 optical microscope. The light source, a Spectra Physics model 2016 5W argon laser, is tuned to the argon green line at 514.5 nm with a power of 100 mW measured as the beam enters the microscope. Laser light is sent through the 100× objective (numerical aperture 0.95) of the microscope and onto the sample surface with a laser spot $<1\ \mu\text{m}$ in diameter. Raman scattered light is collected from a sample volume of a few cubic micrometers, which permits data collection on single crystals as small as $4\ \mu\text{m}$ in diameter. The Raman signal is collected through the 100× objective in a 180° collection geometry and passed through the entrance slits (all slits open to $300\ \mu\text{m}$) into the 1m-focal-length double monochromators of the U-1000 spectrometer. The holographic gratings within the spectrometer are controlled by a dedicated IBM-AT personal computer and the ISA Prism software package, and are stepped in 2cm^{-1} increments. Photon counts are accumulated by an RCA photomultiplier tube for 10 s at each step over the spectral range $100\text{--}1500\ \text{cm}^{-1}$. Data are stored and displayed by the computer. When feasible, spectra are taken from different crystallographic orientations on the same crystal in order to obtain reference spectra that can be compared with those of nonisotropic samples of unknown orientation. The laser Raman microprobe has distinct advantages over its macro-oriented predecessors in this type of study. The Raman microprobe can collect these data in a completely nondestructive manner on samples as small as a few cubic micrometers, with a greater signal-to-noise ratio, and can do so in situ with little or no sample preparation.¹ These qualities allow Raman microspectroscopy to be easily combined with other microbeam techniques in the study of zeolites (see Williamson et al., in this volume) or other minerals.

Discussion

As can be seen in Fig. 1, the Raman bands observed for zeolites in this study are almost completely restricted to the $<600\text{cm}^{-1}$ structurally sensitive region of the spectrum. This restriction implies that differences seen in the spectra of these aluminosilicate framework minerals can be related to differences in their structure. Indeed, these zeolites can be separated into different structural groups sharing common secondary building units (SBUs) that correlate with groupings based on similar Raman spectral signatures (Table 2). However, any band assignments in this region are empirical by nature as the state of theoretical

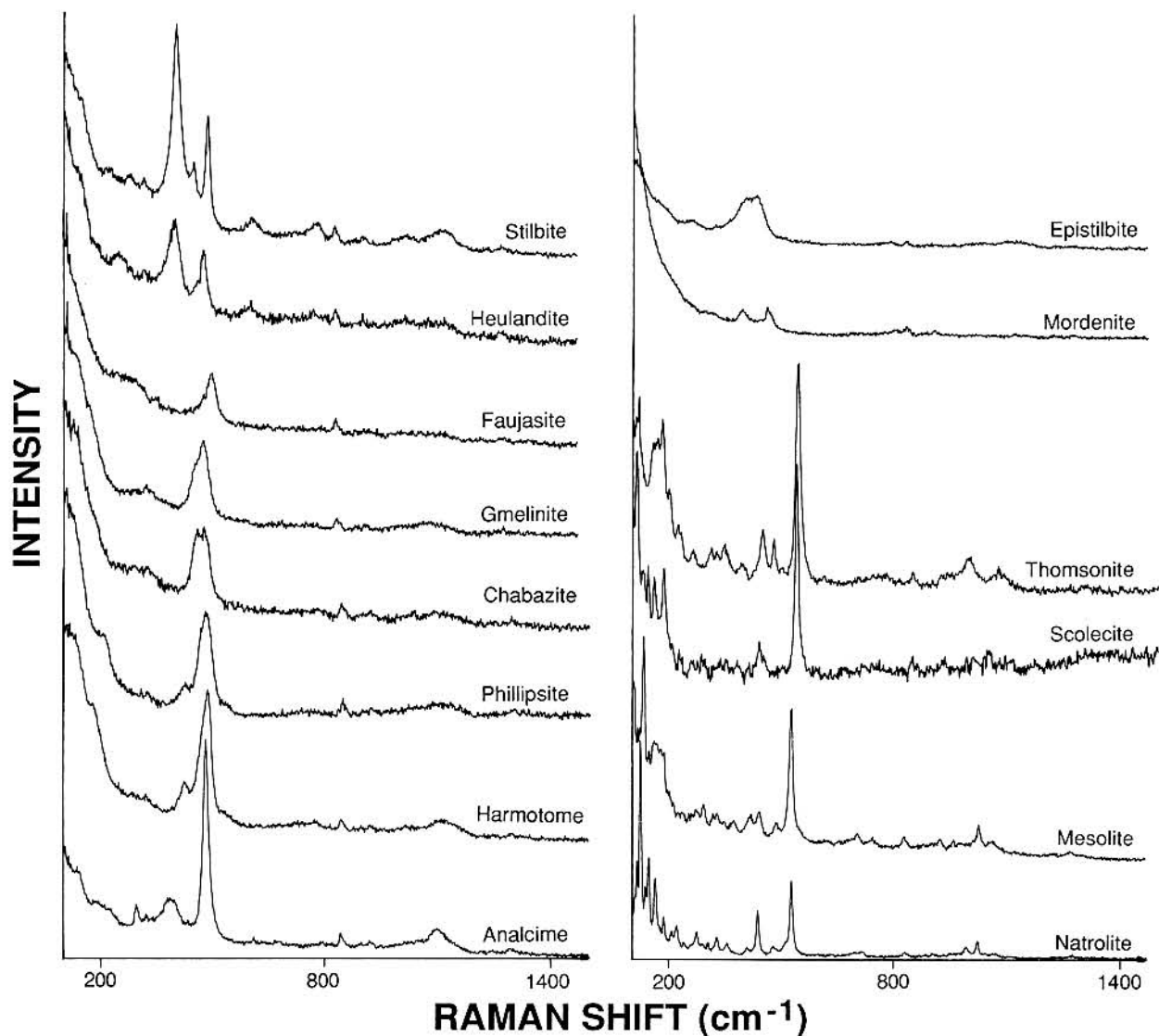


FIG. 1.--Raman spectra of several natural zeolites over 100-1500 cm^{-1} range.

TABLE 2.--Structural group, space group, and characteristic observed Raman frequencies for several natural zeolites.

SBU	Space group	Mineral	Characteristic Raman frequencies (cm^{-1})				
S4R	Ia3d	Analcime	389m	482vs			
	$P2_1/m$	Phillipsite	424m	479vs			
	$P2_1/m$	Harmotome	426m	483vs			
P6R	$R\bar{3}m$	Chabazite	322w	468s			
	$P6_3/mmc$	Gmelinite	324w	473s			
	Fd3m	Faujasite	322w	505s			
4-4-1	Cm	Heulandite	405vs	484s	614m		
	$F2/m$	Stilbite	410vs	496s	618m		
4-1	Fdd2	Natrolite	123vs	145s	163s	443s	534s
	Fdd2	Mesolite	130vs	162m	186m	448m	534vs
	Cc	Scolecite	111vs	142s	158s	436m	536vs
	Pnn2	Thomsonite	116s	156m	180s	446m	539vs
5-1	Cmcm	Mordenite	398m	468m			
	$C2/m$	Epistilbite	408m	436m			

prediction of the Raman activity of zeolites has barely begun to progress beyond isolated TO_4 band assignments.²

Analcime, harmotome, and phillipsite are structurally composed of single rings of four tetrahedra (S4R) and share a common spectral signature of a very strong band centered at 480 cm^{-1} accompanied by a lesser peak or shoulder at 425 cm^{-1} (389 cm^{-1} for analcime). Based on the work of Galeener on silicate-ring vibrations in this structurally sensitive region, one may assign the 480 cm^{-1} band to a planar 4-fold ring stretch in which the vibration is a result of a breathing motion of the oxygen atoms in the planar rings.³ Among these three spectra, it is interesting to note the sharpness of the 480 cm^{-1} peak in analcime (space group Ia3d), and the relative broadening of this peak in the lower-symmetry members of this structural group, harmotome and phillipsite (space group $P2_1/m$). The position of the lower frequency peak at 389 cm^{-1} in analcime as compared to the 425 cm^{-1} peak of harmotome and phillipsite serves to distinguish

analcime from the other members of its group. Harmotome and phillipsite, which share a common structure, have nearly identical Raman spectra, and cannot reliably be distinguished from each other.

Chabazite, gmelinite, and faujasite, structurally characterized by double six-membered rings of tetrahedra (D6R) linked by S4R, are spectrally identified by a broad band (or grouping of bands) centered in the range of 470-510 cm^{-1} assigned to 6-fold and 4-fold ring stretching,¹⁻³ accompanied by a small, broad peak centered at 323 cm^{-1} which is tentatively ascribed to 6-fold ring stretching based upon the inverse relationship between ring size and stretching-mode frequency observed by Galeener.³ As seen in Fig. 1, the strong bands shift to higher frequencies and become sharper with increasing symmetry within this group: the band centered at 468 cm^{-1} in chabazite (space group R $\bar{3}$ m) shifts to 473 cm^{-1} in gmelinite (space group P6 $_3$ /mmc) and to 505 cm^{-1} in faujasite (space group Fd $\bar{3}$ m).

Zeolite species structurally characterized by the "stilbite unit" (4-4-1) can be distinguished from other structural groups by the presence of two strong bands at 410 cm^{-1} and 496 cm^{-1} for stilbite (space group F2/m) and 405 cm^{-1} and 484 cm^{-1} for heulandite (space group Cm), and a third, weak band at \sim 615 cm^{-1} for both minerals.

The natrolite structural group, typically fibrous minerals comprised of chains of tetrahedra (4-1), is the most Raman active group among the natural zeolites. All members of this group exhibit several strong, sharp peaks. Most prominent characteristic of the group are (1) a very strong peak in the range of 110-130 cm^{-1} , (2) a grouping of strong peaks in the range of 145-185 cm^{-1} , and (3) a moderate peak and strong peak at 443 cm^{-1} and 534 cm^{-1} , respectively, for natrolite (space group Fdd2), 448 cm^{-1} and 534 cm^{-1} for mesolite (space group Fdd2), 436 cm^{-1} and 536 cm^{-1} for scolecite (space group Cc), and 446 cm^{-1} and 539 cm^{-1} for thomsonite (space group Pnn2).

The Raman spectra of mordenite and epistilbite, structurally composed of 5-membered rings of tetrahedra with an additional single tetrahedron (5-1), display two moderate peaks. Epistilbite (space group C2/m) displays a broad feature in which at least two peaks are discernible at 408 cm^{-1} and 436 cm^{-1} . The higher-symmetry mordenite (space group Cmcm) displays two moderate peaks at 398 cm^{-1} and 468 cm^{-1} . The \sim 400 cm^{-1} band in each case is assigned to a 5-fold ring stretch.⁵ Although the Raman spectrum of mordenite is very similar in shape and position of the two main peaks to that of heulandite, the mordenite spectrum lacks the 615 cm^{-1} peak characteristic of the stilbite group. Likewise, the spectrum of epistilbite resembles that of chabazite in the D6R group. However, the peaks for epistilbite occur at lower frequencies than the comparable peaks of chabazite or any other member of the D6R group.

All spectra contain a band at \sim 845 cm^{-1} , which has been assigned to silicon-nonbonded

oxygens at the crystal surface, and nearly all display features in the 950-1250 cm^{-1} range ascribed to the zeolite-Si-O-Al-chain asymmetric stretching modes.^{2,6}

Conclusions

Raman spectra of the 14 natural zeolites examined permit their classification by structural group based on SBU type and, in most cases, by individual mineral name. Although relationships can be seen between zeolite structure and Raman spectra, the lack of theoretical interpretation of this low-frequency region places severe restrictions on the interpretation of the spectral features. It is hoped that continuing data collection in this field will provide impetus for further development of theoretical models.

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