

NOTE**Characterization of Zeolites by Infrared Spectroscopy**

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Various infrared bands assigned to microporous molecular sieve zeolites is described.

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The mid-infrared spectra have been considered for the zeolites characterization. The preliminary interpretation of the infrared spectra suggests specificity for zeolite structure type, group and for secondary building units like double rings and large pore openings. The major structural groups present in zeolites can be detected from their infrared patterns. The infrared spectrum in the region of 1500-400 cm^{-1} is a fingerprint of the region indicating structural features of zeolite frameworks.

The infrared spectra of zeolites in the 1300-400 cm^{-1} region appear to consists of two classes of vibrations: (i) those caused by internal vibration of the framework TO_4 tetrahedron, the primary building units (PBU) in all zeolite frameworks, which tend to be sensitive to variation in framework structure, (ii) vibration related to external linkage between tetrahedral units which are sensitive to the framework structure and to the presence of secondary building units (SBU) and building blocks of polyhedra such as rings and pores¹ (Table-1).

TABLE-1
INFRARED ASSIGNMENTS TO ZEOLITES

Internal tetrahedra	Assignment (cm^{-1})	External linkages	Assignment (cm^{-1})
Asym. stretch	1250-950	Double ring	650-500
Sym. stretch	720-650	Pore opening	420-300
T-O bend	500-420	Sym. stretch	820-750
		Asym. stretch	1150-1050 sh

The sharp peak around 1100 cm^{-1} is usually noticed in zeolites. Such an IR peak may be exclusive feature of zeolites that contain the hydrated triple crankshaft chains. The strongest vibration in this region is assigned to a T-O stretch involving motions primarily associated with oxygen atoms or alternatively described² as an asymmetric stretching mode $\leftarrow\text{O T}\rightarrow\leftarrow\text{O}$. The exact position of the Si-O varies with the sum of electronegative groups tend to pull electrons from the cations, thus competing with the bond weakening tendency for the double oxygen to attract electrons, resulting in stiffer Si-O bond and a higher frequency. The Si-O frequency is sensitive to substitution. The presence of an OH or an NH group in the vicinity of a Si-O group generally lowers the stretching frequency by $50\text{-}80\text{ cm}^{-1}$ due to the hydrogen bonding. The broad band around 1100 cm^{-1} has been assigned to the asymmetric stretching of SiO_4 tetrahedra³. The shift to higher wave number is due to the presence of large amounts of other cations, since the Si-O bond distance is shorter than Al-O. The presence of a weaker shoulder at *ca.* 1000 cm^{-1} is assigned to vibration involving $\equiv\text{Al-OH}$ nests created by the cation vacancies. In the region of 750 cm^{-1} and below there are many differences in the number and frequency of the absorption, reflecting the variation in framework composition. The absorption peaks at $750\text{-}700\text{ cm}^{-1}$ corresponds to the symmetric stretching vibration of SiO_4 groups. The bands around 649 , 544 and 468 cm^{-1} are related to bending vibration of SiO_4 groups or in the vibration modes of the 4-membered rings of silicate chains. The stretching vibration of SiO_4 are shifted towards lower frequency indicating that the presence of the internal Si-O...HO-Si bonds.

Stretching modes involving motions primarily associated with the T-atoms, or alternatively described as symmetric modes $\leftarrow\text{O T O}\rightarrow$ are assigned in the region⁴ of $820\text{-}650\text{ cm}^{-1}$. The symmetric stretch modes are further classified into an internal tetrahedral stretch in the lower spectral region of $720\text{-}650\text{ cm}^{-1}$ and external linkage symmetric stretch reflecting structure-sensitive external linkages in the higher region of $820\text{-}750\text{ cm}^{-1}$. The weak absorption at about 650 cm^{-1} is due to the interaction between alumina tetrahedra of the zeolite structure and Al^{3+} . There is splitting of the peak at this region is due to higher O-Si-O angles in the structure⁵. The concentration of small nuclei formed during the induction period can be followed using the intensity of lattice vibration around 558 cm^{-1} . This vibration increases obviously, which shows the increase in the number of double rings of T-atoms.

The symmetric TO_4 stretching region in the spectrum and sharp medium bands around 541 and 472 cm^{-1} . These absorptions either due to TO_4 bending or the motion of the external linkage of the AlO_4 and SiO_4 tetrahedra. The weak band at $1480\text{-}1380\text{ cm}^{-1}$ may be affected by the excess alumina present in the pores. The broad weak band around 4000-

3000 cm^{-1} is attributed to the stretching vibration of hydrogen group of water molecules and amines present in the pores of the zeolites. The weak and sharp peaks in 1700-1500 cm^{-1} resulted due to bending vibration of water.

The external linkage frequencies occur principally in two regions of the spectrum, 600-500 cm^{-1} . A medium intensity band in the former has been related to the presence of double ring polyhedra in the framework. Thus, all of the zeolite frameworks with D-4 and D-6 rings have a medium (or in a few cases mw or ms) band in the 550 cm^{-1} region. The second main external linkage frequency assigned to a breathing motion of the isolated rings forming pore opening in zeolites.

The OH stretching modes at wave numbers of 3626 cm^{-1} with a shoulder at 3600 cm^{-1} is due to two different Brönsted sites, as well as 3678 cm^{-1} (Si-OH) and 3743 cm^{-1} (Al-OH). Various authors assign the band at 3660 cm^{-1} to the OH groups associated with extra framework Al species and the band at 3690 cm^{-1} to another type of Al-OH species.

(i) OH band around 3740 cm^{-1} is due to occluded OH-groups in the zeolite surface. (ii) OH band around 3650 cm^{-1} is due to non-acidic OH groups probably attached to $[\text{AlO}]^+$ entities. (iii) OH band around 3610 cm^{-1} is due to the acidic OH groups.

In condensed phase spectra, amine, templates or structure directing agents show bonding around 3400 cm^{-1} and in dilute solution a bond near 3600 cm^{-1} corresponds to free structure directing agents or templates. Since templates are less electronegative than oxygen, hydrogen bonds in templates are weaker and the shifts in frequency are also correspondingly less.

In interpreting framework structure characteristics of zeolites from IR spectra, it is important that the overall pattern in the spectrum be considered as well as those external linkage regions. Slight structural difference often can be detected by the asymmetry of the bands. Common types of zeolites have similar spectral characteristics such as internal tetrahedral mode less sensitive to framework structure variation, it nevertheless show some structural specificity.

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