Structure-sensitive Raman Bands in Hydrated Zeolite A

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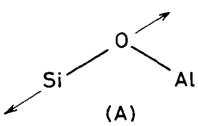
Raman bands that are characteristic of the motion of the oxygen atoms in different environments in zeolite A have been assigned.

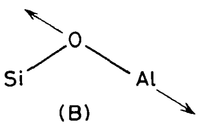
This communication reports Raman spectroscopic data on hydrated zeolite A, and by taking advantage of sub-partitioning of cations, band assignments have been made for structural units and sites in this zeolite. Knowledge of structure, site position, and migration of cations in zeolites is necessary for understanding their function. *X*-Ray diffraction is undoubtedly the major source of structural information about zeolites,[1—5] however, dynamic information about the migration of cations or the formation of zeolites in solution must rely on other methods. We have demonstrated here that vibrations of the aluminosilicate framework of the zeolite involve motion of the oxygen atoms and these are sensitive to their immediate environment. In the case of zeolite A, the structural symmetry introduces three different environments for the oxygen atoms and we can assign Raman bands corresponding to the motion of each of these atoms.

A pseudo unit cell of zeolite A comprises of an $Al_{12}Si_{12}O_{48}^{12-}$ anion framework, with alternate SiO_4 and AlO_4 tetrahedra bonded through corner-sharing oxygen atoms (denoted as $M_{12}A$ where M^+ is a monovalent cation and A represents the aluminosilicate framework of a pseudo unit cell). Upon inspection of a unit cell, it is obvious that three distinct types of oxygen atom surround each Si(Al), and they have been labelled O(1), O(2), and O(3). The O(1)Si(Al)O(2) framework forms the eight-membered ring (site S1), O(2)Si(Al)O(3) forms the six-membered ring (sites S2, S2*, and S2′) and O(1)Si(Al)O(3) forms the four-membered ring (site S3). Since the exchangeable cations



(A)

Si-O stretch



(B)

Al-O stretch

interact with these oxygen atoms, vibrations sensitive to the motion of these atoms are of immediate interest.

Raman spectroscopy has provided useful information about the microstructure of solids such as vitreous silica[6] and aluminosilicate glasses[7] and this provides a convenient starting point for interpreting the Raman spectra of zeolites. In vitreous silica, which is a three dimensional network of SiO_4 tetrahedra polymerized by corner-sharing oxygen atoms, both experimental[8,9] and theoretical analysis[10,11] of the Raman spectra suggest the presence of two groups of bands, which primarily involve oxygen motion. The band observed at 437 cm^{-1} for vitreous silica corresponds to the motion of the oxygen atom in a plane perpendicular to the Si $\cdots$ Si axis. The high frequency bands, observed at 1060 and 1200 cm^{-1} correspond to the asymmetric motion of an oxygen atom along the Si $\cdots$ Si direction. These bands are sensitive to both Si–O–Si bond angle and Si–O bond length. In zeolite A, the interaction will be between neighbouring SiO_4 and AlO_4 tetrahedra, and the coupling can be expected to be considerably smaller than the two SiO_4 tetrahedra in vitreous silica. Even though Al and Si have similar masses, typically the Si–O bond length in zeolite A is 1.608 Å as compared to the Al–O bond length of 1.728 Å.[1] Also, the Al–O bond is considerably more ionic. So, as a model, we can treat the framework vibrations as primarily centred on SiO_4 and AlO_4 tetrahedra modified by a perturbation due to their coupling. In the extreme case, the motion of the oxygen atoms in the plane of the Si–O–Al unit can be described as shown in (A) and (B).

Figure 1(a) shows the Raman spectrum of hydrated $K_{12}A$. In an earlier study, we pointed out the similarity in the Raman spectra of $Na_{12}A$, $K_{12}A$, and $Tl_{12}A$ and their difference from $Li_{12}A$.[12] Three bands are observed between 900—1200 cm^{-1} and can be assigned to the Si–O stretch. The position of these bands will be influenced by the Si–O force constants, an approximate idea of which can be obtained from the Si–O bond lengths. Single crystal *X*-ray diffraction studies of hydrated $Na_{12}A$,[1] $K_{12}A$,[4] and $Tl_{12}A$[5] show in general that the Si–O(2) bond length is shorter than the Si–O(1) and Si–O(3) bond lengths. Also, the Si–O(2)–Al angle (typically 160°) is usually greater than the other two angles (typically 145°).[1,4,5] The central field model[10,11] suggests that as the Si–O–Al angle will increase, so will the coupling leading to a higher stretching frequency. This suggests that the Si–O(2) stretch will occur at the highest frequency. We assign the bands at 962, 1032, and 1095 cm^{-1} to Si–O(3), Si–O(1), and Si–O(2) stretching motions, respectively. The choice of Si–O(3) as the lowest frequency is based on the fact that in general it has a longer bond length than Si–O(1). It is important to point out that bond lengths are only an approximate measure of force constants.

The Al–O stretch is observed around 650—750 cm^{-1}. Only two bands are observed at 694 and 735 cm^{-1} instead of the three bands due to the three different oxygen atoms. Since the Al–O bonds have smaller force constants, it is expected that the separation in frequencies will be less marked than for Si–O. Gramlich and Meier's[1] diffraction data indicates that the Al–O(1) band is the shortest and would therefore be responsible for the 735 cm^{-1} band.

The symmetric motion of the oxygen atom contributes to the strong band at 487 cm^{-1}. The absence of any splitting indicates that this bending motion is not sensitive to the different oxygen atoms. The average Si(Al)–O bond lengths and bond angles will influence the peak position of this band. Since bending force constants have lower magnitudes, their sensitivity to geometric factors is considerably diminished as compared with stretching force constants.

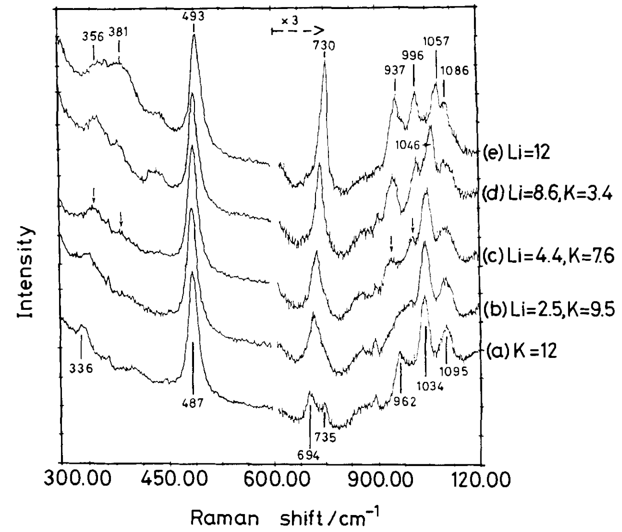


Figure 1. Raman spectra of $K_{12}A$ (a) exchanged with Li^+ ions. The compositions are shown on the right. Completely exchanged $Li_{12}A$ is shown in (e). Laser line 457.9 nm. Slit width 6 cm^{-1}. Laser power 150 mW at the sample.

In $Li_{12}A$, Figure 1(e), four bands are observed in the high frequency region. We have previously suggested that upon exchanging Li^+ into zeolite A, the framework is distorted from cubic symmetry.[12] We were led to this conclusion by the bands at 356 and 381 cm^{-1} which exactly coincide with the i.r. bands.[13] The exact nature of this distortion is unclear, because no *X*-ray diffraction studies have been carried out on $Li_{12}A$. But it seems from the Raman spectra that, upon Li^+ exchange, the Si–O(3) stretch splits into two bands at 937 and 996 cm^{-1}. Also the Si–O(2) stretch has decreased in frequency indicating a decrease in Si–O(2)–Al angle and *vice versa* for Si–O(1), which suggests a larger Si–O(1)–Al angle.

To confirm these assignments, we took advantage of the sub-partitioning of cations in the different zeolite sites.[14] Typically, in hydrated $Na_{12}A$, $K_{12}A$, and $Tl_{12}A$, seven to eight cations per unit cell are close to the six-membered rings (S2, S2*, S2′) and three to four cations occupy S1 (eight-membered rings).[1,4,5] The cations in site S2 preferably interact with the O(3) atoms, whereas those in site S1 interact with the O(1) and O(2) atoms. Our strategy was to prepare zeolite A with varying amounts of two monovalent cations and examine if there were any preferential interactions with various oxygen atoms.† The notable changes occur in the high frequency Si–O stretching region, since these vibrations are most sensitive to the cations' interaction with the sites.

Figure 1 shows the Raman spectra of $K_{12}A$ on progressive exchange with Li^+ ion. At the composition, $Li_{2.5}K_{9.5}A$, the only spectral change is the disappearance of the 962 cm^{-1} band [Si–O(3)] indicating that the first few Li^+ ions are preferentially replacing K^+ ions from site S2. Upon increasing

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† Ion exchange was carried out for 6 h by stirring completely exchanged zeolite ($M_{12}A$) with varying concentrations of the exchanging cation. The time allowed for exchange was enough to attain equilibrium as verified by Raman and atomic fluorescence spectroscopy.

the Li^+ ion concentration to 4.4 ions per unit cell, new bands are observed at 356, 381, 937, and 996 cm^{-1} [Figure 1(c), indicated by arrows]. As discussed earlier, the appearance of these bands indicates a distortion of the zeolite framework. This structural distortion continues upon further ion-exchange, and at $Li_{8.6}K_{3.4}A$, the Si–O(1) band shifts from 1034 to 1046 cm^{-1} and the Si–O(2) band at 1095 shifts to 1086 cm^{-1}. The only difference in the Raman spectra between $Li_{12}A$ and $Li_{8.6}K_{3.4}A$ is the position of the Si–O(1) band at 1046 cm^{-1}. This suggests that the last 3—4 K^+ ions are interacting with the Si–O(1) group and must be held in site S1 positions.

As expected, the opposite sequence of events is observed upon exchanging $Li_{12}A$ with K^+ ions. The first 3—4 K^+ ions only affect the 1056 cm^{-1} band (S1 sites), whereas upon further exchange, the 962 cm^{-1} band grows in intensity as site S2 is filled.

We have obtained similar results for the Li^+–Na^+ system, except that the partition equilibrium constants tend to be larger for Na^+ than for K^+. Exchange isotherm studies have shown[15] that an inflection is observed at a population of 4—5 Li^+ ions per unit cell. We suggest, from the above mentioned results, that this effect arises from the framework structural distortion that occurs when more than four Li^+ ions are exchanged into the zeolite. It is of great interest to see if the predictions based on Raman spectroscopy will be verified by single crystal *X*-ray diffraction studies on $Li_{12}A$.

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