Investigation of the Influence of the Cations on Normal Modes of Y Zeolites: Vibrational Studies and Computer Simulations

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A comparison of experimental and calculated vibrational spectra of alkali-metal zeolites is made.

Zeolites are widely used as heterogeneous catalysts and their chemical and physical properties are known to be significantly influenced by the extra-framework cations. Therefore, ion exchange in aqueous solution as well as in the solid state, have been extensively studied.[1] Among other methods including MAS NMR and XRD, vibrational spectroscopic techniques have proved to be very useful tools for the characterization of the zeolite framework and the detection of charge-balancing cations at specific sites. The essential step in interpreting vibrational spectra is the assignment of experimentally obtained bands to normal modes. As this can not easily be achieved on a purely empirical basis, computer simulation techniques, such as molecular dynamics[2,3] and normal coordinate analyses[4] have been used to elucidate the problem of framework and cation vibrations in the vibrational spectra of zeolites. Different interpretations have been reported. Ozin and coworkers[5] made an empirical assignment of bands in the far-IR region to specific cation sites, assuming the framework to be rigid during the cation movements and the cations to vibrate independently from each other. However no correlations between cation sites and vibrational frequencies were found in molecular dynamics simulations.[2] From the theoretical point of view the movement of the cations should not be independent due to the Coulomb interaction expressed by corresponding force constants. Moreover, a coupling of low frequency lattice modes such as torsion with cationic vibrations should be observable because of their comparable force constants. In this study, experimental and calculated vibrational spectra of alkali-metal zeolites are presented and compared. The kinetic energy distributions are calculated to examine the assignment of experimental frequencies to normal modes, especially in the far-IR.

The starting material for all alkali-metal Y zeolites was $Na_{55}Y$ (Si/Al = 2.5). Ion exchange with KBr, RbCl and CsCl was performed using two different methods, solid-state ion exchange and conventional ion exchange in aqueous solution. Far-IR spectra were recorded using activated self-supporting wafers, while mid-IR spectra of dehydrated samples were measured in different matrices (NaCl, KBr, RbCl, CsCl). Raman spectra of the zeolite powders as such were obtained on a Perkin-Elmer System 2000R NIR-FT Raman spectrometer using a Nd-YAG laser with a wavelength of 1064 nm and a power of 1000 mW.

In order to calculate the vibrational spectra, lattice energy minimizations at constant pressure followed by eigenvalue calculations in Cartesian coordinates have been carried out for NaY, KY, RbY and CsY using the computer program METAPOCS[6,7] on a Convex C 120. The force field consisted of four types of potentials: (*i*) a Buckingham potential $[E_{ij} = A_{ij}\exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6]$, (*ii*) a spring potential describing the core shell interaction $(E_i = \frac{1}{2}K_iR^2)$, (*iii*) a three-body $[E_{ijk} = \frac{1}{2}k_{ijk}(\Theta - \Theta_0)^2]$ and (*iv*) a Coulomb potential $(E_{ij} = q_iq_j/r_{ij})$.

Table 1 Experimental and calculated lattice constants (*a*) of cation-exchanged Y zeolites

Zeolite	$a_{\text{exptl.}}$/Å	$a_{\text{calc.}}$/Å
$Na_{48}Y$	24.759	24.660
$K_{48}Y$	24.774	24.879
$Rb_{48}Y$	24.786	24.930
$Cs_{48}Y$	24.784	24.991

The parameters are taken from refs. 8–13. The long-range Coulombic part of the potential is computed using the Ewald summation method,[14,15] the minimization method used was the Newton–Raphson algorithm. The relevant system to describe the vibrational properties of a cubic face-centred lattice is the Bravais cell, *i.e.* the primitive unit cell containing only one quarter of the cubic unit cell.[16] The Bravais cell (one double sodalite unit), containing 96 oxygen atoms, 36 silicon atoms, 12 aluminium atoms and 12 cations, was used as the simulation box. The normal modes, part of the METAPOCS output, are used to compute IR and Raman intensities using the procedure described by Creighton *et al.*[17] implemented in our own code.

The lattice energy minimization leads to reasonable structures with regard to symmetry and geometry. In Table 1 lattice constants of the optimized geometries are shown along with experimental results obtained by powder X-ray diffraction of the hydrated samples described above. As expected the lattice constant increases with increasing cation radius, although the effect is smaller in the experimental data. This is due to hydration of the samples and incomplete cation exchange especially for Cs^+.

The calculated and experimental IR and Raman frequencies of the solid-state ion-exchanged alkali Y zeolites are summarized in Tables 2 and 3. The conventionally exchanged samples show the same trends during cation exchange, although the observed frequency shifts are smaller because of the lower extent of exchange. In the mid-infrared spectra frequency shifts

Table 2 Experimental and calculated frequencies (cm^{-1}) in the IR spectra of solid-state cation-exchanged Y zeolites

NaY		KY		RbY		CsY	
exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.
—	—	1159sh	—	1158sh	—	1151s	—
1035vs	985s	1026vs	987s	1025vs	980s	1011vs	974s
798m	784s	792m	764s	792m	757s	788m	753s
588m	594m	579m	588m	582m	584m	577m	584m
—	—	509m	505m	511m	505m	511m	505m
479s	468s	466s	438s	466s	416s	467s	425s
318vw	326vw	315vw	329vw	317vw	329vw	320vw	331vw
272vw	279vw	270vw	283vw	270vw	256vw	272vw	258vw
189w	197w	194sh	198w	195vw	—	180vw	162vw
159sh	180sh	131w	171w	—	140w	95vw	128vw
100vw	107w	107vw	93w	97w	76w	60vw	68w

Table 3 Experimental and calculated frequencies (cm^{-1}) in the Raman spectra of solid-state cation-exchanged Y zeolites

NaY		KY		RbY		CsY	
exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.
1105w	1037vw	1118w	1039w	1113w	1038w	1107w	1028w
837w	814w	830w	819w	833w	812w	834w	836vw
800vw	769w	796vw	771w	800vw	774vw	800vw	778vw
503vs	496vs	496vs	501vs	499vs	504s	500vs	501s
—	—	478sh	453vs	477sh	458vs	477sh	458vs
432sh	433w	—	—	435sh	—	—	—
361vw	361w	358w	374w	357w	372w	354w	374w
302m	282w	294m	296w	297m	265w	299m	264m

up to 24 cm^{-1}, especially in the stretching region, are observed. Furthermore an additional band at 510 cm^{-1} appears in the mid-IR region of KY, RbY and CsY.

The calculated vibrational spectra show a satisfactory agreement with the experimental spectra. The frequencies and intensities of the far-IR region are reproduced particularly well. The simulated Raman spectra, particularly the most intense band at about 500 cm^{-1}, are also in good agreement with the experimental spectra. This leads to the conclusion that the shell model with its ionic force field terms is a reasonable model for the simulation of vibrational spectra. Differences in the mid-IR spectra, in particular above 900 cm^{-1}, are thought to be due to an insufficient description of the covalent part of the Si–O and Al–O bonds by the shell model as reported by van Santen and co-workers.[12] The calculated spectrum of sodium Y zeolite is shown in Fig. 1 with the experimental IR spectrum for comparison. The results for KY, RbY and CsY are of the same quality.

In order to get information about the nature of the normal modes especially in the far-IR, the kinetic energy distribution (KED) of NaY has been calculated.[18] The percentage of the sodium ion movements compared to the total kinetic energy is shown in Fig. 2.

As can be seen, the kinetic energy of the cations in the vibrational modes above 250 cm^{-1} amounts to less than 1% of the total. Since the participation of the cations is close to zero in the high frequency region, it follows that the observed shifts due to cation exchange in the valence stretching range are due to changes in the lattice parameters. No coupling with the cation modes is discernible. The normal modes below 250 cm^{-1} consist mainly of cation vibrations. For some modes, up to 80% of the total kinetic energy originates from the cation movements. These bands can only be attributed to cation vibrations. Normal modes with less than 1% of the kinetic energy attributable to the cations are assigned to lattice vibrations near 150 cm^{-1}. Moreover, these results are supported by IR investigations of ^{18}O isotopic-exchanged sodium zeolite Y. In the mid-IR all bands are significantly shifted to lower wavenumbers due to ^{18}O exchange (except the band near 800 cm^{-1}), while in the far-IR shifts are only observed above 240 cm^{-1}. Calculations of the KED of cations on different sites (SI, SI′, SII, SII′) show a simultaneous participation of all cations during the normal modes. This leads to the conclusion that no assignment of observed far-IR bands to individual sites can be made. This is contradictory to the findings of Ozin and coworkers.[5] Although each cation site shows a characteristic frequency pattern, there is always a superposition of bands in the experiments and a coupling of cation motions at different sites in the calculations. Thus no characteristic group frequencies for individual cation sites could be observed. These results support the conclusion of MD simulations[2] that no band can unambiguously be attributed to one cationic site.

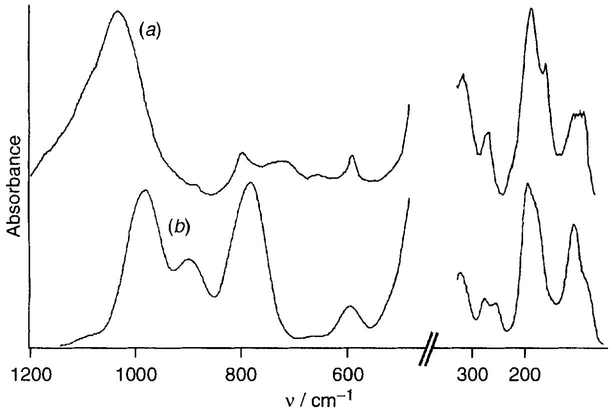

Fig. 1 Experimental (*a*) and calculated (*b*) IR spectra of sodium zeolite Y

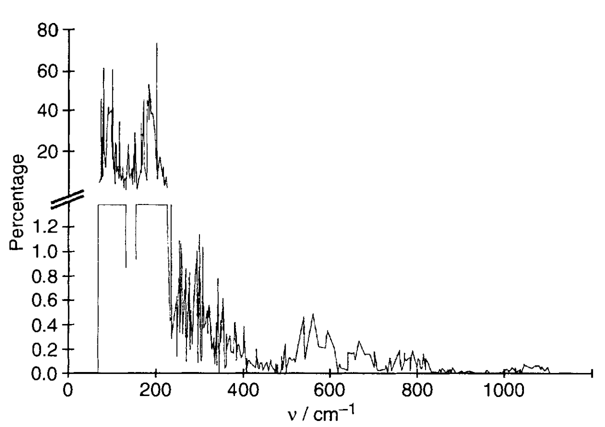

Fig. 2 Kinetic energy distribution of sodium ions in sodium zeolite Y

More detailed results on this topic will be published in the near future, including a comparison with Raman spectra of ^{18}O-exchanged Y zeolites and a dicussion about the improvement of the calculated spectra in the mid-IR by adding valence force-field terms.

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