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LATTICE RELAXATION OF ZEOLITES *

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Quantum-chemical cluster calculations as well as solid-state chemical lattice-calculations indicate that zeolitic SiO_2- and $AlPO_4$-structures are flexible structures. The structures reflect the subtle balance of electrostatic and covalent interactions. The different electrostatic interactions lower the symmetry of layered $AlPO_4$-structures compared to that of the corresponding SiO_2-compounds. The result is a smaller zeolite-channel dimension for the $AlPO_4$-structure compared to that of the corresponding SiO_2-network. Deprotonation of the zeolite-lattice leads to large local changes in geometry that changes acidity compared to that predicted for a non-flexible lattice. Changes in lattice vibrational frequencies are consistent with the theoretically predicted relaxation of the zeolite-lattice.

Keywords: Cluster calculations for zeolite structures, flexible zeolite structures, deprotonation induced restructuring of zeolites

1. Introduction

One of the major results of recent computational-chemical studies on zeolites is evidence of the flexibility of the zeolite-lattice. Next to the rich topology of edge-connected tetrahedral frameworks [1], to which class the zeolite lattice belongs, the flexibility of the oxygen-bridge connecting the tetrahedra is an important feature determining structural as well as chemical properties of zeolites.

Here we will discuss its consequences for the relative stability of zeolites and Brønsted acidity.

One of the earliest quantum-chemical studies simulating mineral-properties using neutral clusters of silica-units is due to Gibbs [2]. He studied the potential-energy surface of the clusters sketched in fig. 1a and noted that a quantum-chemical calculation of the [Si–O–Si] cluster using a minimum basis set gave a minimum-energy at a bond angle of 144°. A value close to that found in α-quartz. This result strongly suggested structure control by covalent local bond-

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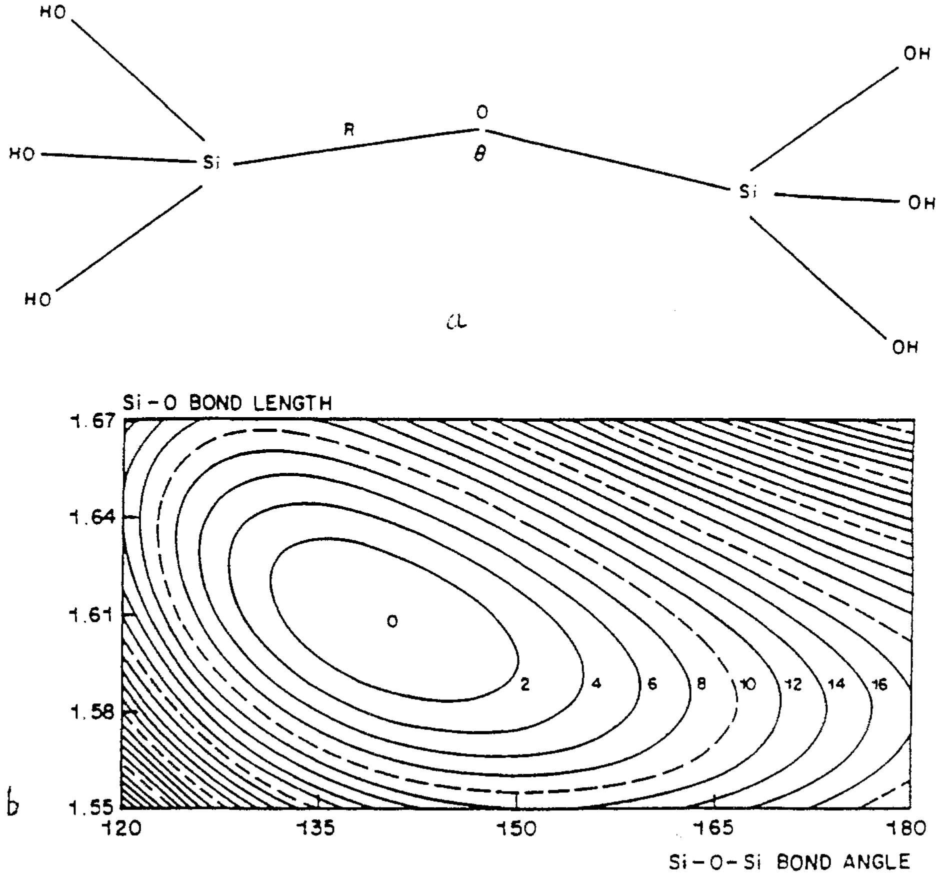


Fig. 1a. Dimer cluster; C_{2v} symmetry assumed. Fig. 1b. Total energy as a function of Si-O bond length and Si-O-Si bond angle. Contour lines in units of kJ/mol.

ing features. Study of the potential-energy surface as a function of bondangle and SiO-bondlength shows a very shallow potential-energy valley when one widens the Si-O-Si angle and at the same time adjusting the SiO bondlength to the corresponding potential-energy minimum. Elsewhere we published a quantum-chemical account of the relative energy-content of three-, four-, five- and six-tetrahedral rings of composition $[(SiO)(OH)_2]_n$ [3]. Essential again is optimisation of the structure for the bending Si-O-Si angle as well Si-O bondlength. As follows from fig. 1b optimisation of only one of the two coordinates results in an energy minimum which may be significantly different from that of the completely geometry-optimised cluster.

One finds as a general result that the bondangles and bonddistances are different in the different ring-systems. The differences in heat of formation are less than a few kJ per mole $SiO(OH)_2$, unless the tetrahedral angles around the silicon-atom de form. Three-rings of tetrahedra require tetrahedral deformation, which results in destabilization with respect to the larger rings. The deformation-energy of the tetrahedral bond is of the order of ~ 10 kJ per mole $SiO(OH)_2$. Notwithstanding important new quantum-chemical developments as the CRYSTAL-program developped by Pisani [4], alternative lattice-mechanics procedures based on the use of classical-mechanical atom-atom potential-energy expressions have to be used, if one wishes to study bulk chemical or physical properties. It appears that these are highly geometry dependent [5].

A significant advance is the availability of potentials that have been developed on the basis of fitting-procedures to cluster potential-energy surfaces generated by ab-initio quantum chemical calculations [6]. Not only for SiO_2 polymorphs, but also for the $AlPO_4$ polymorphs and alumino-silicates partial-charge rigid-ion potentials are now available.

Elsewhere the application of these potentials has been extensively analysed [6] for silica polymorphs and alumino-silicates.

A major result of these calculations is confirmation of the idea of lattice-relaxability, also for the extended structures. Calculations on the lattice-stability of many different silica-polymorphs show that, when the structure is well optimised and no three-rings are contained in the structure, the formation energy varies not more than ± 10 kJ per mole SiO_2. This result suggests that the thermochemistry of silicon-rich zeolitic structures is controlled by interaction with the molecules that during synthesis become enclosed in the channels of the material [7].

These calculations also provide an interesting insight into the relative importance of electrostatic versus covalent interactions in structure stability. For the silica-polymorphs an analysis will appear in [8]. Here we will illustrate this issue for the $AlPO_4$ polymorphs.

For catalysis acidic protons bonded to the zeolite lattice are important. Due to their presence zeolites can be used as solid acid catalysts [9].

Quantum-chemical cluster calculations [10] indicate two important features. The strongly acidic proton is the one bonded to the oxygen atom connecting a silicon and aluminum containing tetrahedron: [Si–O-Al]. The lower valency of the aluminum atom enhances the proton-oxygen atom interaction compared with the [Si–O–Si] system. Coordination to Al^{3+} weakens the OH bond compared to that of the free silanol group. The $[Al–(O–)_3]^+$ group can be considered a Lewis-acid promoting the acidity of the proton.

The second important feature is the large change of the optimised geometry of protonated dimers compared to non-protonated dimers. This is illustrated in fig. 2. The optimised geometry corresponding to the geometrical energy minimum of a protonated cluster in the presence and absence of a base (NH_3) is shown. Comparison is also made with a deprotonated anionic cluster. The Si and Al valencies have been saturated with hydrides. The geometry-optimised clusters are the result of ab-initio calculations involving apt basis sets [11].

Lattice-energy minimisation-studies by Kramer [6c] have shown that structure-relaxation due to protonated oxygen-atoms bridging Si- and Al-tetrahedra in faujasite is considerable and comparable to that in clusters. This

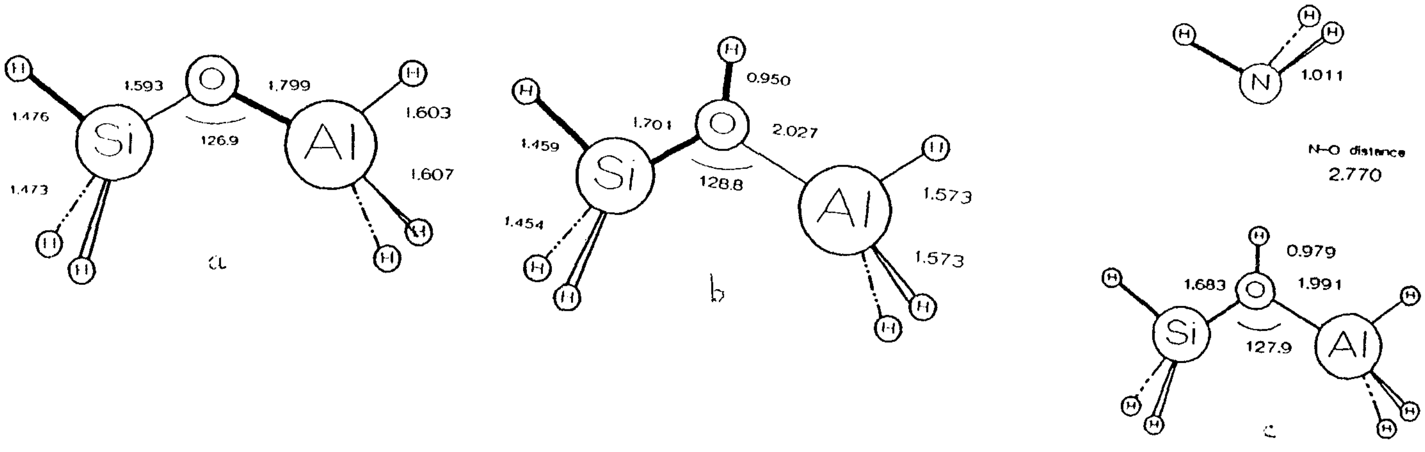


Fig. 2. Optimised geometry for the anionic cluster (a), the protonated cluster (b) and for NH_3 hydrogen-bonded to the protonated cluster (c).

contrasts with earlier suggestions of lattice-rigidity [12]. Its consequences for Brønsted acidity in zeolites are analysed in the third section.

2. Lattice-energy minimization studies of $AlPO_4$ polymorphs

The procedure to determine the classical-mechanical lattice potentials for lattice-energy minimization studies involves a choice of the oxygen, aluminum and phosphorus charges. These can only be determined if potentials are not only the result of a fitting procedure to ab-initio cluster calculations, but parameters are further refined by comparison with predicted solid state chemical properties [6a,6b].

The potential-forms used are an electrostatic Coulomb interact ion, dependent on charge choice and a short-range Buckingham type potential involving a repulsive as well as attractive potential energy-term. For many charge choices acceptable fits to quantum-chemically generated cluster potential-energy surfaces can be found. Fig. 3 shows bulk compressibility values predicted for energy-minimised $AlPO_4$-polymorphs of different connectivity. Calculations have been performed with oxygen-potentials similar to those of the SiO_2 system, but the aluminum and phosphorus charge-difference is considered to be a parameter dQ. One notes a very interesting sudden change in bulk-compressibility once dQ exceeds a particular value. This occurs especially for the layered $AlPO_4$ structures, where the bulk-compressibility jump corresponds to a structure change. Comparison with measured bulk-compressibility of berlinite [13] and experimentally determined structures of $AlPO_4$-8 [14] leads to the conclusion that $dQ \geqslant 0.6$. This is a very interesting result. The topology of $AlPO_4$- and SiO_2-polymorphs can be the same, but because $dQ \neq 0$, the structure of the $AlPO_4$-polymorph becomes deformed. The structural-change is illustrated for the layered $AlPO_4$-5 structure in fig. 4. Also for the $AlPO_4$-5 structure a local minimum can be found close to that of the corresponding high symmetry structure of its SiO_2-polymorph SSZ-24. Computation of the vibrational frequencies of $AlPO_4$-5 in this local energy-minimum results in real as well as imaginary frequencies. It implies that this local minimum of the $AlPO_4$-5 structure corresponds to a saddle-point on its multi-dimensional potential-energy surface and is non-stable. In fig. 4 a real mode and imaginary-mode is shown. Clearly the imaginary destabilising mode corresponds to a displacement of the layers. The stable energy-minimum of the $AlPO_4$-5 structure is found allowing for the displacement of the lattice layers. This result is very general for the layered $AlPO_4$-structures. Recently it has been experimentally confirmed for $AlPO_4$-8 [14].

The layer-displacements shown for VPI-5 in fig. 5 have an important consequence for the channel-dimensions of the $AlPO_4$-polymorphs compared to their SiO_2 analogues. The channel-dimensions of the $AlPO_4$-polymorphs decrease, compared to the dimensions found for the high-symmetry SiO_2-polymorphs.

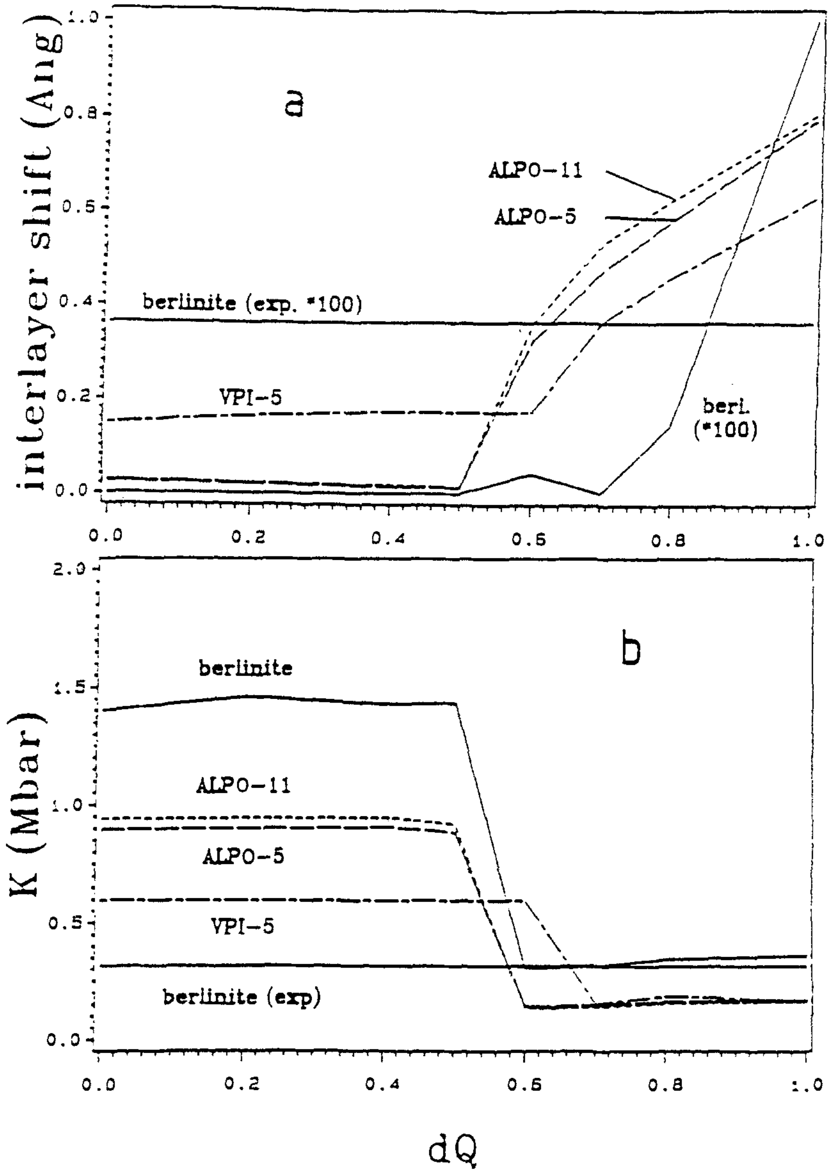


Fig. 3. Simulated powder diffractograms for VPI-5, based on the calculated structures for different dQ-values (a). For reference we show the experimental diffractogram together with the refinement of Crowder et al. [15].

Indeed the experimentally observed pore-dimensions of VPI-5 are less than predicted on the basis of the high-symmetry form considered originally [15].

The explanation for the layer-displacements is the change in balance of electrostatic interactions and covalent interactions with dQ. The shift in layers and corresponding increase volume-density is counteracted by the repulsive tetrahedral interactions but favoured by the attractive electrostatic terms linear in

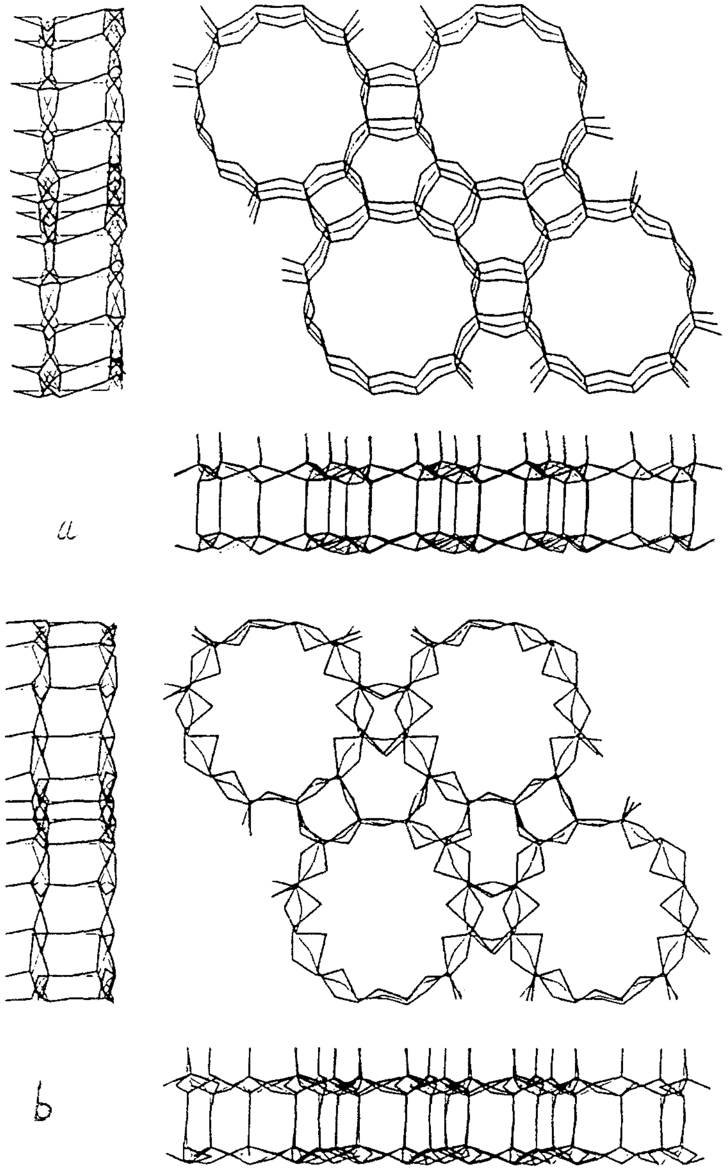


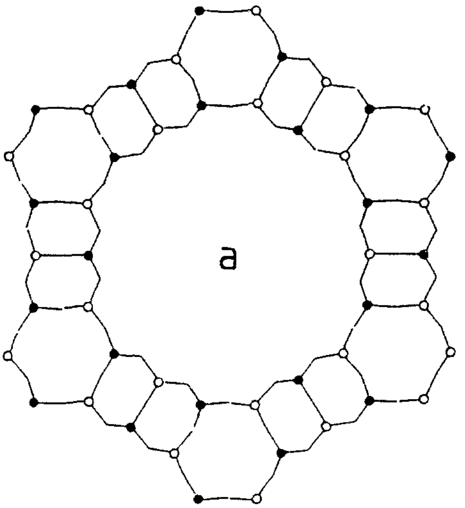
Fig. 4. Two calculated vibrations of relaxed $AlPO_4$-5 structure: a) imaginary mode (24 cm^{-1}); b) real mode (332 cm^{-1}). Thin line: equilibrium structure. Thick lines: structure deformed by vibration (arbitrary amplitude).

dQ. The repulsive interaction between neighbouring Al- and P-containing tetrahedra decreases with dQ^2.

It is interesting to note that similar as in the case of the SiO_2-structural deformations larger electrostatic interactions result in highly symmetric structures.

3. Brønsted acidity

A schematic energy-diagram of the changes in energy of a [Si–O–Al] dimer upon deprotonation is shown in fig. 6. The most important feature of the potential-energy dependence is the different change of the potential-energy with the distance Al–O for the non-protonated cluster (R_A) compared to that of the protonated cluster (R_H). It has a very important consequence for acidity. Let us initially suppose the cluster to be embedded in a zeolite-lattice and that the potential energy-surface is not significantly affected by this.



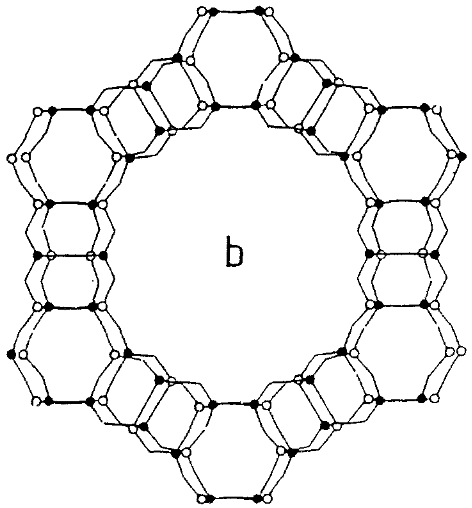


Fig. 5a. The structure as predicted for the SiO_2-form with the layers on top of each other. Fig. 5b. The structure as predicted for the $AlPO_4$-VPI-5 compound.

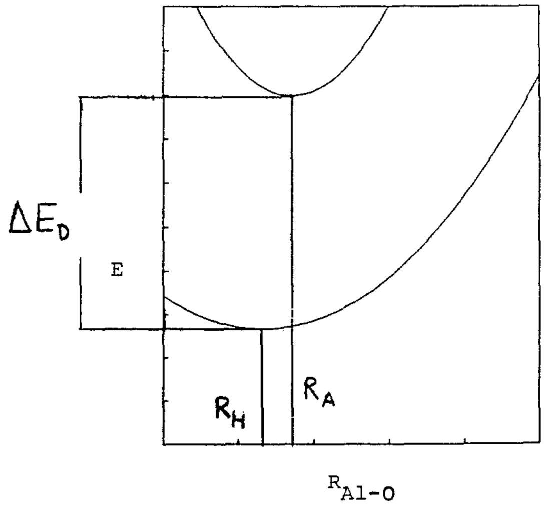


Fig. 6. Potential curves for the protonated and non-protonated cluster as a function of the distance Al–O (arbitrary units).

We will first discuss the case of a completely rigid-lattice and then analyse what happens in a completely flexible lattice. In a rigid lattice acidity will depend on the Si–Al distance, or equivalently the Si–O–Al angle of the oxygen-bridge considered. The dependency of the acidity on the Si–Al distance will be based on the dependence of the acidity of the Al–O distance (fig. 6). In a rigid lattice the Al–O distance will be the same in the deprotonated and in the protonated form. For distances $R_A > R_H$ (fig. 6) the energy differences between the two curves will decrease and the proton behaves chemically as an intrinsically stronger acid. When the system is allowed to completely relax one value for acidity is found, that relates to the energy-difference $E_A - E_H$. At present no calculations are available that give $E_A - E_H$ as a function of ring-size or composition. This is subject to ongoing research. For actual calculations applicable to flexible systems these considerations imply that only energy-differences are relevant derived from completely geometry optimized structures. Geometry-optimisation for the protonated as well as the nonprotonated cluster is required. If the deprotonation energy is calculated in a fixed geometry a biassed value for the deprotonation energy will be found.

Lattice-calculations on the faujasite structure [6c] indicate significant flexibility of the zeolite lattice. The degree of flexibility of a zeolite-lattice may be a function of lattice-position as well as zeolite connectivity. For example in dodecasil-type lattices very large Si–O–Si angles are observed [16]. It seems likely that relaxation on these positions is restricted and a high Brønsted acidity would be predicted for protons coordinated to such sites. One has to realize however that the proton tends to bind to these oxygen-atoms that allow for smaller [Si–O–Al] angles.

Recently Catlow a.o. [17] have experimentally demonstrated that upon dehydration of Ni^{2+} exchanged zeolite Y, part of the Ni^{2+} ions move inside the double-six rings. The positive charge of the Ni^{2+} ions attracts negatively charged oxygen ions, but repulses positively charged lattice-cations. The double-six ring deforms significantly due to the presence of the Ni^{2+} ion. This is indicative of the large flexibility of the faujasite-lattice, even when a significant concentration of Al-ions is present.

Interestingly geometry-optimised quantum-chemical cluster calculations of Na^+ with negative charged Al-containing three-rings showed the same phenomenon [5c].

Experimental indications that lattice-relaxation of the zeolite lattice occurs when the proton reacts whith a base, derive from recent experiments of the proton-NH_3 interaction. Fig. 7 shows a comparison of the infrared transmission spectrum due to the lattice modes of protonated zeolite Y in the absence [7a] and presence [7b] of adsorbed NH_3 [18]. Around 800 cm^{-1} and 1050 cm^{-1} one observes an upward shift in frequency when ammonia is desorbed. The lattice frequency around 580 cm^{-1} is found to be significantly suppressed. The frequencies of the modes infrared active around 800 cm^{-1} derive from symmetric combinations of [Si–O–Al] stretch modes, the corresponding asymmetric modes

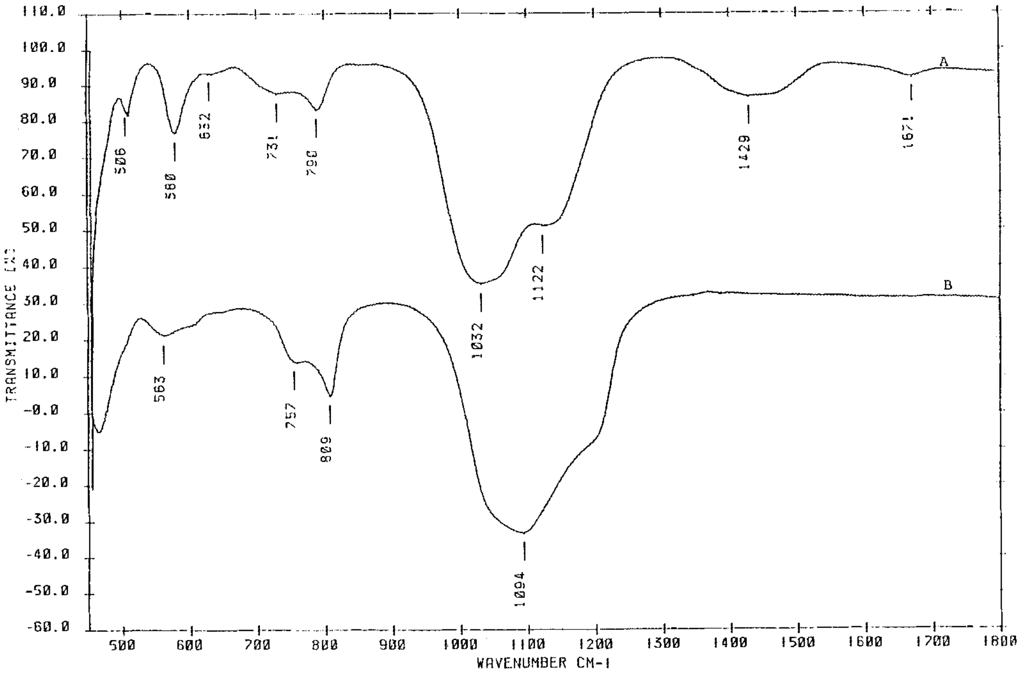


Fig. 7. Infrared transmission spectra of NH_4Y (a) and HY (b).

are the vibrations observed around 1050 cm^{-1}. The difference in frequency between the symmetric and asymmetric modes is approximately proportional to $\nu_0 \cos \theta$ [19]. Here ν_0 is the average frequency of Si–O and Al–O modes. When the angle θ decreases the splitting between asymmetric and symmetric mode-frequencies decreases. This has been theoretically predicted [10e] and is observed upon protonation of the faujasite lattice.

The average upward shift of the stretch-frequencies is the result of a decreased bondstrength of Si–O and Al–O bonds next to protonated oxygen-atoms and increased bondstrengths of neighbouring non-protonated Si–O and Al–O bonds. Because of bondorder-conservation the weakening of one bond is compensated for by a strengthening of neighbouring bonds [5c].

The mode at 580 cm^{-1} can be assigned mainly to the motion of oxygen atoms that share sodalite and double-six ring tetrahedral four-rings [20]. The change in intensity seems to indicate that four-rings have the weaker acidity.

Neutron-scattering experiments by Stucky [21] and Jobic [22] also contain evidence of changes in lattice mode frequency when protonated and deprotonated lattices are compared.

Finally a short comment has to be made on the interaction of ammonia with the zeolitic proton. The calculations by Teunissen et al. [11] show that ammonia coordinates to the proton bonded to the bridging oxygen-atom (fig. 8a), rather by

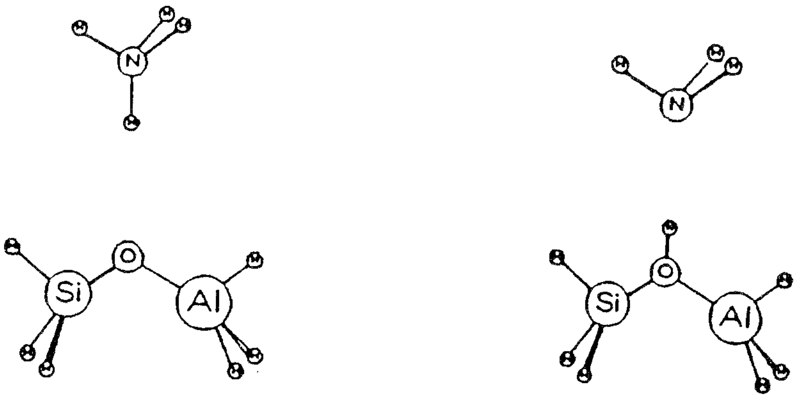


Fig. 8. The hydrogen bonded (a) and the ionic (b) structures.

way of an extremely strong hydrogen-bond than by proton-transfer and formation of an ammonium ion (fig. 8b). In the hydrogen-bonded form the proton-oxygen atom interaction is significantly weakened (the frequency is found to decrease by 550 cm^{-1}). Ongoing investigations intend to demonstrate whether ammonium-ions become stable relative to the hydrogen bonded form when an adsorption geometry is chosen such that the ammonium-ion becomes stabilized by coordination to several lattice oxygen-atoms. Stabilization of ammonia in high-coordination adsorption states has been suggested by Pelmenschikov [23].

The cluster-calculations suggest that if not a stable adsorption-state hydrogen-bonded ammonia may be the transition-state of desorbing or adsorbing ammonia. The hydrogen-bonded form of mono-coordinated ammonium is ~ 50 kJ/mol more stable than the charge separated ammonium form. Interestingly Rees a.o. [24] recently observed that the rate of adsorption of ammonia from zeolite Y is accompanied by a negative activation energy.

Possibly the complex (fig. 2d) is the transition-state for desorption from the mobile NH_4^+ ground state. Loss of rotational motion in the transition state results in a loss of entropy $\sim R$ comparable to that experimentally found.

Elsewhere [5b,5c] we discussed whether the dominance of covalent-bonding in the zeolite-framework is consistent with the experimentally observed dependence of intrinsic acidity on zeolite composition [25]. These changes are found to be important only when the composition of the tetrahedra in the second coordination-sphere with respect to the proton is changed. Indeed the principle of bond-order conservation predicts a weaker acidity with increasing next-nearest T-site occupation of an aluminum ion [5c]. The weaker aluminum-oxygen bond results in an increased next-neighbour silicon-oxygen bond. This in turn weakens the other silicon-oxygen bond to which the proton is bonded. The overall effect is a stronger proton-bridging oxygen interaction.

4. Conclusion

Theoretical and experimental evidence converges towards the conclusion that the zeolite-lattice is highly flexible, due to the low torsional and bending frequencies of the [T–O–T] bond. When the topology of the network requires adaptation of bond lengths and angles, T–O–T angle and bond-length changes are preferred over deformation of the tetrahedra. Rather wide [T–O–T] angles may result with little loss in stability.

We have discussed for the $AlPO_4$ lattice that the difference in charge between the aluminum and phosphorus containing tetrahedra reduces the repulsive electrostatic interaction between neighbouring tetrahedra and results in layer-displacements in layered $AlPO_4$ compounds.

As long as overall neutral local configurations are considered also electrostatic effects are local and of a short-range. This is the basis of the result that end-on bonded ammonia prefers the hydrogen-bonded mode rather than the charge separated ammonium form.

In a flexible lattice interaction of protons with a basic adsorbate results in a local adjustment of the geometry when proton transfer occurs. Experimentally this is observed by a change of the vibrational frequencies of the zeolite-lattice modes.

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