

# Bridging hydroxyl groups in zeolitic catalysts: a computer simulation of their structure, vibrational properties and acidity in protonated faujasites (H-Y zeolites) <sup>☆</sup>

Klaus-Peter Schröder, Joachim Sauer <sup>1</sup>

*Zentralinstitut für physikalische Chemie, Rudower Chaussee 5, O-1199 Berlin, Germany*

Maurice Leslie

*Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK*

C. Richard A. Catlow and John M. Thomas

*Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK*

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The structure and properties of the four possible bridging hydroxyl groups in silicon-rich H-faujasite (zeolite Y) are studied by lattice-energy minimization carried out within the classical shell model. The most likely proton-accepting sites are the O1 and O3 oxygens. Their hydroxyl stretching frequencies are shown to be responsible for the characteristic high-frequency (HF) and low-frequency (LF) bands, respectively, in the infrared spectra of H-faujasites. The variation of the OH stretching frequencies for the four isolated sites is correlated with changes of local geometry such as the O-H bond length and the Si-O(H)-Al and the Si-O-H angles. However, there appears to be no correlation with differences in the acid strength as evidenced by the values of the calculated deprotonation energy of the O(1)H and O(3)H hydroxyl groups for which only a minor difference is predicted.

## 1. Introduction

Zeolites of the faujasite structure are among the most widely investigated and commercially important catalysts and molecular sieves. Their Brønsted acidity arises from bridging hydroxyl groups. The siting and structure of the latter are the subject of intensive research. Two main types of bridging hydroxyl groups give rise to two different bands in the infrared spectrum of H-faujasite, the so-called high-frequency (HF) and low-frequency (LF) bands at 3610–3650 and 3550 cm<sup>-1</sup>, respectively. Although, for a finite Si-Al ratio, both may be composed of a variety of subbands [1,2], there is general agreement that hydroxyl groups at the O1 position (lo-

cated in the supercage) are responsible for the HF band, whereas the LF band corresponds mainly to O3H hydroxyl groups in the sodalite cage [3–9]. Although the siting of the bridging hydroxyl groups is well understood, a full description of their local geometry which takes lattice relaxation into account is not yet available. X-ray and neutron diffraction cannot easily distinguish between Si and Al atoms and the relatively low concentration of hydroxyl groups raises further difficulties. The structural model emerging from spectroscopic techniques [5,10] is still incomplete. Quantum-chemical structure predictions by ab initio methods [11,12] are limited to relatively small molecular models which are not specific for individual frameworks and, thus, neglect environmental effects.

Lattice-energy minimization methods using analytical potential functions have proved successful in predicting structures and properties for a variety of silicates and zeolites [13–19]. Their use for proton-

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<sup>1</sup> Also with BIOSYM Technologies Inc., San Diego, California, USA.

ated forms of zeolites is hampered, however, by the problem of deriving suitable and reliable potentials. Here we report results for bridging hydroxyl sites in faujasite which are obtained with new hydroxyl oxygen parameters. The agreement of the average of the predicted structures with *ab initio* results on relatively small models [12] was used as a criterion for assessing the empirical potential. We note that a potential has been recently reported for hydroxyl groups in zeolites which is largely derived from *ab initio* data, but which treats the hydroxyl group as a pseudo-lattice oxygen atom [20]. The results in this paper suggest that it is possible to model OH groups explicitly.

## 2. Potentials

Our study uses potentials that combine long-range electrostatic with short-range pair interactions. The long-range Coulomb term uses formal charges and the short-range two-body term is of the Buckingham type,

$$V_{ij}^{\text{short}} = A_{ij} \exp(-r_{ij}/\rho) - c_{ij} r_{ij}^{-6}. \quad (1)$$

Additionally, a three-body bond-bending term is used for O-Si-O groups,

$$V_{ijk}^{\text{bend}} = k_{ijk} (\theta_{ijk} - \theta_{ijk}^0)^2. \quad (2)$$

To allow polarization of the oxygen ions, the shell model is adopted. This describes the polarizable atom in terms of a core (in which the mass of the atom is concentrated) and a shell (describing the polarizable valence-shell electrons) which are connected by a harmonic spring. The superiority of the shell over the rigid-ion model in predicting the structure of zeolites has been recently demonstrated [14,19].

The treatment of hydroxyl groups requires some modifications in the approach. Fractional charges are used for the hydroxyl oxygen and hydrogen and their short-range interaction is described by a Morse function derived from quantum-chemical results [21].

The same parameters as recently used by Jackson and Catlow [13] and Winkler et al. [18] were chosen (table 1). The parameters stem mainly from empirical fitting to structural and physical properties of  $\alpha$ -quartz and  $\text{Al}_2\text{O}_3$ . They were previously used successfully to simulate structure and properties of dif-

Table 1  
Potential parameters <sup>a)</sup>

Buckingham potential			
	<i>A</i> (eV)	$\rho$ (Å)	<i>C</i> (eV Å <sup>6</sup> )
Si <sup>4+</sup> ...O <sup>2-</sup> <sup>b)</sup>	1283.907	0.32052	10.66158
Al <sup>3+</sup> ...O <sup>2-</sup>	1460.3	0.29912	0.0
O <sup>2-</sup> ...O <sup>2-</sup>	22764.0	0.149	27.88
Si <sup>4+</sup> ...O <sup>1.4-</sup>	983.5566 <sup>c)</sup>	0.32052	10.66158
Al <sup>3+</sup> ...O <sup>1.4-</sup>	1142.6775 <sup>c)</sup>	0.29912	0.0
O <sup>2-</sup> ...O <sup>1.4-</sup>	22764.0	0.149	27.88
O <sup>2-</sup> ...H <sup>0.4+</sup>	311.97	0.25	0.0
Morse potential			
	<i>D<sub>e</sub></i> (eV)	$\alpha$ (Å <sup>-1</sup> )	<i>r<sub>0</sub></i> (Å)
O <sup>1.4-</sup> ...H <sup>0.4+</sup>	7.0525	2.1986	0.9485
Three-body potential			
	<i>k</i> (eV rad <sup>-1</sup> )	$\theta_0$ (deg)	
O-T-O <sup>d)</sup>	2.09724	109.47	
Core-shell			
	<i>k</i> (eV Å <sup>-2</sup> )		
O <sup>2-</sup>	74.92		

<sup>a)</sup> Refs. [13,18].

<sup>b)</sup> Charges (*e*): Si<sup>4+</sup> 4.0, Al<sup>3+</sup> 3.0, H<sup>0.4+</sup> 0.426, O<sup>1.4-</sup> -1.426, O<sup>2-</sup> 0.86902, O<sup>2-shell</sup> -2.86902.

<sup>c)</sup> This work, fitted to quartz and sillimanite.

<sup>d)</sup> O stands for O<sup>2-</sup> and O<sup>1.4-</sup>, T for Si<sup>4+</sup> and Al<sup>3+</sup>.

ferent zeolites [13-17]. First tests showed, however, that an unreasonable structure of bridging hydroxyl groups is predicted, when the Si<sup>4+</sup>...O<sup>2-</sup> and Al<sup>3+</sup>...O<sup>2-</sup> short-range parameters are also used for the interaction of the hydroxyl oxygen with the Si<sup>4+</sup> and Al<sup>3+</sup> ions. Si-O and Al-O distances of 189 and 199 pm, respectively, are obtained, which are in conflict with values of 170 and 194.5 pm predicted from quantum-chemical *ab initio* calculations on small clusters [12]. Sim and Catlow [22] also calculated T-O distances that were too long in their study of hydroxyl groups compensating the charge of an aluminium defect in  $\alpha$ -quartz. The reason is obviously that the short-range potential and the reduced electrostatic interaction due to the fractional charge of -1.426 adopted for the hydroxyl oxygen are not in balance. Hence, there was a need to derive short-

range  $A$  parameters that are specific for the  $\text{Si}^{4+} \dots \text{O}^{1.4-}$  and  $\text{Al}^{3+} \dots \text{O}^{1.4-}$  interactions. However, the only data available are the experimental structure and properties of  $\alpha$ -quartz and sillimanite, respectively. Therefore, an auxiliary fractional-charge model was constructed for these materials that is in accord with the stoichiometric relations,

$$q_{\text{O}} = -\frac{1}{2}q_{\text{Si}}, \quad (3)$$

and

$$q_{\text{O}} = -\frac{2}{3}q_{\text{Al}}, \quad (4)$$

respectively, and at the same time mimics the magnitude of the electrostatic interaction between the hydroxyl oxygen and the  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  ions, respectively:

$$(+4)(-1.426) = q_{\text{O}}q_{\text{Si}} = -2q_{\text{O}}q_{\text{O}} \quad (5)$$

and

$$(+3)(-1.426) = q_{\text{O}}q_{\text{Al}} = -\frac{3}{2}q_{\text{O}}q_{\text{O}}. \quad (6)$$

This yields a fractional-charge model with

$$q_{\text{O}} = -\sqrt{2 \times 1.426}, \quad (7)$$

$$q_{\text{Si}} = -2q_{\text{O}}, \quad (8)$$

and

$$q_{\text{Al}} = -\frac{3}{2}q_{\text{O}}, \quad (9)$$

which is used only for deriving the specific  $A$  parameters needed. In the case of sillimanite, different parameters were allowed for tetrahedrally and octahedrally coordinated aluminium. In this way, short-range parameters were obtained, which are consistent with the electrostatic interaction of formally charged Si and Al ions with hydroxyl oxygen of the fractional charge of  $-1.426$ . No reference is made to observed data on zeolites, but, as shown below, the structure predictions for bridging hydroxyl groups in zeolites are substantially improved.

### 3. Calculations

The calculation of minimum lattice-energy structures can be done either with constant volume (i.e. only the atomic positions are optimized) or constant pressure in which the unit-cell parameters are in-

cluded in the optimization. We used the latter in the present study, employing the computer code THBREL [23]. The long-range electrostatic contribution to the lattice energy was determined using the Ewald summation. The cut-off radius for the short-range interaction was  $7.5 \text{ \AA}$ .

It is well established that bridging hydroxyl groups are formed between Al and Si atoms [24]. Since all T sites in faujasite are equivalent, there are only four possible bridging hydroxyl groups for a large Si/Al ratio corresponding to protonation of the O1, O2, O3 and O4 oxygens as shown in fig. 1. After an initial minimization of aluminium-free faujasite, one  $\text{Si}^{4+}$  ion per unit cell was substituted by  $\text{Al}^{3+}$  and one of the neighbouring oxygen ions was protonated. We used the smallest-possible unit cell with  $a=b=c \approx 17.2 \text{ \AA}$  and  $\alpha=\beta=\gamma=60^\circ$ ; therefore, the Si/Al ratio was 47. The structures were fully relaxed and the harmonic stretching frequencies  $\omega_{\text{OH}}$  were calculated. The results are summarized in table 2,

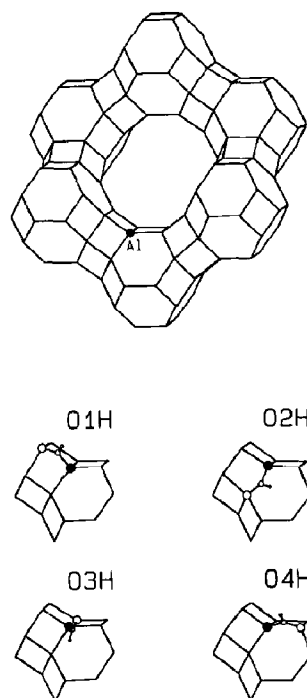


Fig. 1. The four different types of bridging hydroxyl groups in silicon-rich faujasite. Top: Location of the aluminium atom within the framework. Bottom: Orientation of the hydroxyl groups formed by adding a proton to the four crystallographically different oxygen atoms.

Table 2

Relative energies and harmonic OH stretching and SiOH bending frequencies of the four bridging hydroxyls in silicon-rich H-faujasite

	$E^{\text{rel}}$ (kJ mol <sup>-1</sup> )		$\omega_{\text{OH}}$ (cm <sup>-1</sup> )		$\delta_{\text{SiOH}}$ (cm <sup>-1</sup> )	
	this work	CNDO/2 <sup>a)</sup>	this work	obs. <sup>b)</sup>	this work	obs. <sup>c)</sup>
O1H	5.3	7	3772	3770 <sup>d)</sup> 3783 <sup>e)</sup>	937	1015
O2H	19.8	39	3702	—	963	—
O3H	0.0	0	3736	3690 <sup>e)</sup>	951	1055
O4H	23.7	58	3751	—	944	—

<sup>a)</sup>  $\Delta H^{\text{rel}}$  estimated on the basis of CNDO/2 calculations on molecular models [26].<sup>b)</sup> Determined using eq. (3) with  $x_{\text{OH}}$  taken from ref. [33]. <sup>c)</sup> Ref. [33].<sup>d)</sup>  $\nu_{\text{OH}}$  taken from ref. [31]. <sup>e)</sup>  $\nu_{\text{OH}}$  taken from ref. [32].

where the energies are reported as relative to that calculated for protonation of the O3 site – the lowest energy configuration.

#### 4. Results and discussion

The calculated relative lattice energies show that O1 and O3 are the preferred sites for protonation, with O3H being slightly more stable. However, the energy difference of about 5 kJ mol<sup>-1</sup> between O3H and O1H is small, so that we expect both hydroxyl groups to be present in H-faujasite. Since the structure after deprotonation and relaxation is the same for the four hydroxyl groups considered, it follows that differences in the calculated energies give directly the differences in deprotonation energies (but have opposite signs). Since the deprotonation energy is a measure of acid strength [24,25], we conclude that the O1H group is slightly more acidic than the O3H group. The proton affinities follow the sequence O3>O1>O2>O4 as previously predicted

by CNDO/2 calculations [26]. Note that all these results refer to a very low concentration of bridging hydroxyl groups.

Table 3 shows the bond distances and angles for all four bridging hydroxyl groups. They are in close agreement with results of quantum-chemical model calculations [12]. In particular, the surprisingly large Al–O(H) distance predicted by the quantum-chemical study is confirmed by our calculations. This structural parameter and the flexible Si–O(H)–Al angle show the largest variation for the four possible bridging hydroxyl groups. The energetically favoured hydroxyl groups, O1H and O3H, have geometries which are closest to the geometry predicted for completely free hydroxyl groups by quantum-chemical calculations. Further support for the reliability of the description of hydroxyl group structures by the lattice-energy minimization calculations is provided by the fact that the average Al–O distance of 174 pm for the whole AlO<sub>4</sub> tetrahedron is close to the value of 173 pm observed for zeolite A [27]. Structural information for bridging hydroxyl

Table 3

Geometries (distances in pm, angles in deg) of the four bridging hydroxyls in silicon-rich H-faujasite

	$r_{\text{OH}}$	$r_{\text{SiO}}$	$r_{\text{AlO}}$	$r_{\text{AlH}}$	$\angle \text{AlOSi}$	$\angle \text{SiOH}$	$\langle r_{\text{SiO}} \rangle^{\text{a)}$	$\langle r_{\text{AlO}} \rangle^{\text{a)}$
O1H	100.0	169.4	191.0	238.6	131.1	123.0	160.3	173.8
O2H	100.4	168.7	190.3	229.6	142.4	117.6	160.7	174.3
O3H	100.2	169.7	193.0	233.2	138.7	120.7	160.7	174.2
O4H	100.1	168.8	190.6	236.3	134.0	121.4	160.3	174.3
q.ch. <sup>b)</sup>	96.4	170.0	194.5	246.1	131.5	117.5	—	—

<sup>a)</sup> Average distance for the whole TO<sub>4</sub> tetrahedron.<sup>b)</sup> Predicted structure on the basis of quantum-chemical ab initio calculations on small models [12].

groups is sparse in H-faujasite. It is known that the Al-H distance, found by Stevenson [5] using  $^1\text{H}$  NMR and later by Freude et al. [10] combining  $^1\text{H}$ ,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  solid-state NMR, is  $238 \pm 4$  pm. Very recently, Al-H distances of  $248 \pm 4$  and  $237 \pm 4$  pm were deduced from the  $^1\text{H}$  MAS NMR sideband patterns of bridging hydroxyl groups O1H and O3H, respectively, in zeolite HY [28], which compare with calculated distances of 239 and 233 pm (table 3). Neutron-diffraction studies on deuterated acidic faujasitic cracking catalysts have directly located ionizable OH groups, with a bond length of  $100 \pm 20$  pm [29] (see also ref. [30]). However, the calculated O-H distances of about 100 pm are clearly too large when compared with accurate ab initio calculations on small models [12]. It seems that the O...H Morse potential employed requires further optimization when used for zeolites.

Table 2 also shows the calculated harmonic frequencies of the OH stretching and SiOH bending vibrations. The higher harmonic stretching frequency  $\omega_{\text{OH}}$  of the O1H bridging hydroxyl group compared with that of the O3H group indicates that the HF band should be assigned to O1H, whereas the O3H group is the source of the LF band. From IR spectroscopy, the HF band is known to lie between  $3610\text{ cm}^{-1}$  [31] and  $3623\text{ cm}^{-1}$  [32] for a Si/Al ratio higher than 7, whereas the LF band lies at  $3550\text{ cm}^{-1}$ . Our results, however, should be compared to the harmonic frequencies  $\omega_{\text{OH}}$ , which are related to the anharmonic fundamental frequencies  $\nu_{\text{OH}}$  by

$$\omega_{\text{OH}} = \nu_{\text{OH}} + 2x_{\text{OH}}. \quad (10)$$

From the observed overtones of the HF and LF vibrations, the anharmonicity constants  $x_{\text{OH}}$  are known to be 80 and  $70\text{ cm}^{-1}$ , respectively [33]. The calculated frequencies lie in the observed range of harmonic frequencies ( $3690\text{--}3783\text{ cm}^{-1}$ ), although the difference between the HF and LF frequencies is somewhat underestimated. Since the anharmonicity constant for the SiOH bend is known to be small [34], the calculated harmonic frequencies can be directly compared with observed fundamentals (table 2). They are somewhat underestimated but the simulation agrees with the experiment in predicting the higher value for the O3H hydroxyl group [33,35]. It is evident that the description of the OH stretching frequencies is clearly better than the prediction of

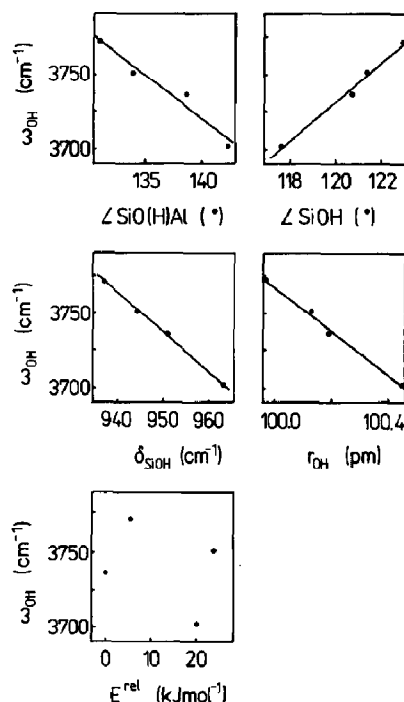


Fig. 2. Relation between calculated harmonic frequencies  $\omega_{\text{OH}}$  and structural, dynamic and energetic properties of bridging hydroxyl groups in H-faujasite.

the O-H distances. However, there is an urgent need for a potential that well describes both the structural and dynamic features of the O-H bond in zeolitic hydroxyl groups, which can only come from further quantum-chemical calculations.

Fig. 2 shows the close correlation between dynamic and structural properties of the bridging hydroxyl groups studied here. The OH stretching frequency increases with decreasing SiOH bending frequency, decreasing O-H distance, decreasing Si-O(H)-Al angle, and increasing Si-O-H angle. Similar correlations were recently suggested by Pel'menschikov et al. [36]. On the other hand, there is no clear relation between the relative energy (and the deprotonation energy) of the bridging hydroxyl group and its OH stretching frequency. This confirms the conclusion from theoretical considerations [25] that the OH band in infrared spectra, although a useful guide as seen from the (Brönsted acid) catalytic activity and the infrared stretching frequencies [35,37] is not, strictly speaking, a proper measure of acid strength.

## 5. Conclusions

The simulation shows that the bridging hydroxyl groups O1H and O3H give rise to the HF and LF bands of H-faujasite, respectively. The difference between their acid strengths measured by the deprotonation energies is minor. There is no experimental evidence which is in conflict with this finding. A strong correlation is found between the vibrational frequencies and structure factors of bridging hydroxyl groups. There have been speculations (e.g. ref. [33]) that a hydrogen bridge of the O3H proton with another oxygen atom might be the reason for the lower frequency of the LF band. We did not find any indication of such a hydrogen bond.

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