Pentacoordinated germanium in AST zeolite synthesised in fluoride media. A ^{19}F NMR validated computational study†

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A computational study shows that Ge is pentacoordinated in the double four rings (D4R) of Si/Ge AST zeolites; the calculated chemical shifts of F-D4R containing 8Si, 7Si1Ge and 8Ge reproduce the trends of ^{19}F NMR experiments.

Microporous oxide materials find applications in catalysis and separations and much effort has been devoted to improving their performance. Starting from aluminosilicate zeolites, formed by microporous corner-sharing tetrahedral frameworks, isomorphous substitution of silicon and/or aluminium has made it possible to span their topologies up to more than 160 different frameworks at present and new types continue to be synthesised at an accelerated pace.[1]

The addition of germania (GeO_2) to the synthesis gel has made it possible to obtain recently new germanosilicate framework types such as IWW,[2] IWR,[3] ITQ-21,[4] UOZ[5] and UTL,[6] and new compositions such as ITQ-29.[7] The trend of germanium towards higher than four coordination makes it important to control the synthesis conditions. Fluoride anions also have a structure directing role, orienting towards frameworks comprising small cages such as $[4^15^26^2]$, $[4^15^6]$ and $[4^6]$ (also called *double four ring* or D4R). The structures so formed crystallise faster than in OH^- media and with essentially no connectivity defects.[8] Studies, most of them with pure silica zeolites, are aimed at characterising the F^- location, and pentacoordinated silicon has been found, amongst others, in $[4^15^26^2]$ cages by ^{19}F NMR techniques.[9]

No pentacoordinated silicon or germanium has been claimed to exist in D4R, and the F^- anion is reported to be in the cavity centre at a Si···F (or Ge···F) distance of 2.6–2.7 Å regardless of the Si/Ge content of the D4R. The ^{19}F NMR spectra of Si/Ge zeolites show peaks at −38, −20 and −16 ppm which are assigned to F^- inside D4R with 8Si, 7Si1Ge and 8Ge respectively.[10,11] We will model different locations of F^- inside the D4R and compare the calculated ^{19}F NMR spectra with the experimentally obtained spectra. The results will be used to suggest the location of F^- inside D4R of composition 8Si, 7Si1Ge and 8Ge, and also to find whether Si and/or Ge forms pentacoordinated species within the D4R of AST zeolite.

The methodology used involves a combination of molecular mechanics and *first principles* techniques. Two models are proposed (Fig. 1). 'Model A' corresponds to that reported in the literature in which the fluoride anions occupy the centre of the D4R. 'Model B' comes from an optimisation of unit cells by molecular mechanics, and subsequent *ab-initio* calculations of the ^{19}F chemical shifts, which has been done as explained below.

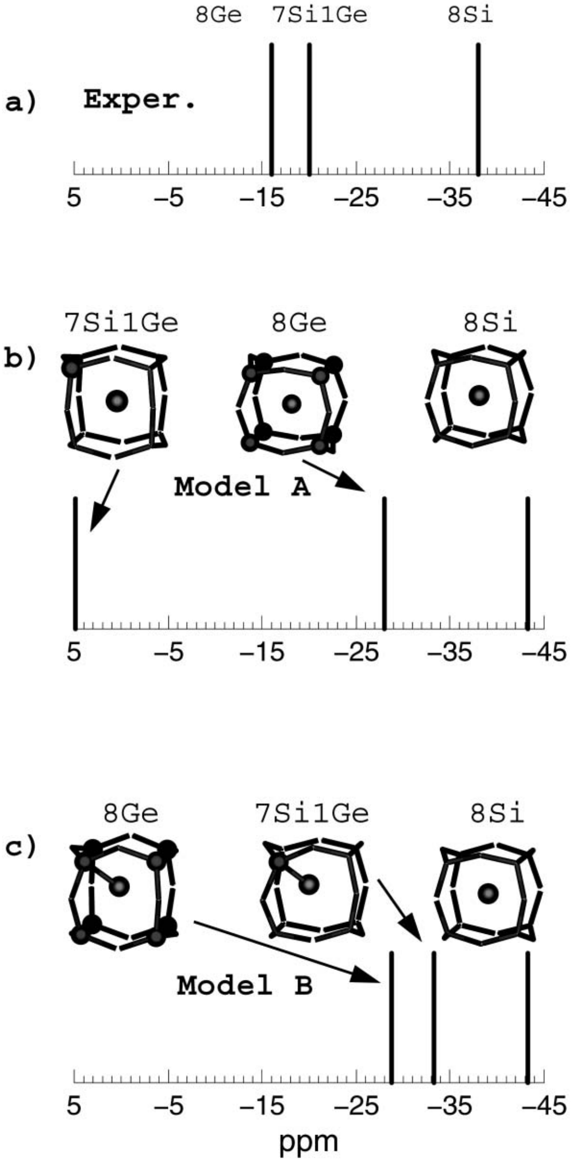

Fig. 1 (a) ^{19}F NMR chemical shifts from experiments in [10,11]; (b) 'Model A', with F^- in the cavity centre, and calculated ^{19}F NMR chemical shifts; (c) 'Model B', with F^- as optimised from the forcefield in [12], and calculated ^{19}F NMR chemical shifts.

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† Electronic supplementary information (ESI) available: cell parameters and atomic coordinates of optimised cells. See http://www.rsc.org/suppdata/cc/b4/b419131e/

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First, a full geometry optimisation of the Si/Ge AST zeolite was performed with an atomistic forcefield for Si/Al/Ge/F zeolites, which gives structural results similar to experimental data.[12] The complete periodic solid is taken into account and the Coulombic interactions are properly treated by an Ewald summation technique. The unit cell is [DABCOH,F]$_2$-$Si_{20-x}Ge_xO_{40}$, where DABCOH is protonated 1,4-diazabicyclo[2.2.2]octane, the organic structure directing agent reported in the synthesis of the pure germania AST zeolite (zeolite ASU-9).[13]

The compositions simulated correspond to $x = 0, 1, 20$. The results with $x = 0$ (octadecasil zeolite) give a tetracoordinated silicon with F^- in the centre of the D4R, as reported in a previous study.[14] For the pure germania case, $x = 20$ (ASU-9), the optimisations give a pentacoordinated Ge (d(Ge–F) = 2.17 Å). For the case $x = 1$ (Fig. 2), a pentacoordinated Ge is also found with Ge–F bond distance 1.89 Å. The Ge–F bond length decreases when less germanium is present due to the larger attractive interaction between nonbonded Ge···F with respect to Si···F. The optimised cells are given as supplementary material.

From these optimised geometries, the D4R are taken to construct clusters terminated by OH, with composition $[Si_{8-y}Ge_yO_{20}H_8F]^-$. The cases $y = 0, 1, 8$ correspond to the D4R previously referred to as 8Si, 7Si1Ge and 8Ge respectively. This is what we call 'Model B' (see Fig. 1).

With 'Model A' and 'Model B' defined, the corresponding ^{19}F chemical shifts were calculated with *first principles* techniques. The NMR chemical shieldings were calculated by the CSGT (continuous set of gauge transformations) method. The exchange-correlation B3LYP functional was selected, and as for the basis sets, 6-31G(2d) for the atoms in the D4R and 6-311G(2d) for the fluoride anion were tested. The basis sets employed include polarisation functions as well as f orbitals in the fluoride anion to give a larger flexibility on this ion, taking into account that chemical shifts are very sensitive to the quality of the basis set.

In order to test this methodology, the case study of zeolite ITQ-13 was chosen. ITQ-13 was synthesised in pure silica form in fluoride media and the location of F^- has been accurately characterised by X-ray microdiffraction techniques.[15] Two ^{19}F NMR signals at −38 and −66 ppm are assigned to fluoride inside D4R and $[4^15^26^2]$ cages respectively. The simulation of the corresponding cages with the *first principles* techniques described above gives chemical shifts of −43.5 and −75.8 ppm respectively. Results within ±10 ppm with respect to the experiments can be considered acceptable.[16,17] Once the methodology has been tested, the results corresponding to 'Model A' and 'Model B' are compared.

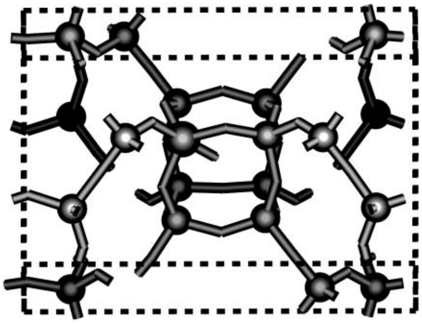

Fig. 2 Optimised unit cell of AST structure [DABCOH,F]$_2$-$Si_{19}GeO_{40}$, with Ge in the D4R, showing the pentacoordinated Ge and the Ge–F bond. The organic moiety has been omitted for the sake of clarity.

Table 1 DFT/B3LYP calculated ^{19}F NMR chemical shifts (ppm) of clusters $[Si_{8-y}Ge_yO_{20}H_8F]^-$ with $y = 0, 1, 8$ denoted by 8Si, 7Si1Ge and 8Ge, respectively. The clusters correspond to 'Model B' in Fig. 1

Basis set[a]	8Si	7Si1Ge	8Ge
B1	−44.3	−34.2	−29.8
B2	−43.3	−33.3	−28.8
B3	−46.7	−33.9	−31.4

[a] Basis set 6-31G(2d) was used for Si, Ge, O, H atoms in all calculations. For F atom 6-311G(2d), 6-311G(2df) and cc-pVTZ basis sets were used which correspond to B1, B2 and B3 basis sets respectively.

It can be seen that 'Model A' (Fig. 1b) fails to reproduce the relative ordering of the experimental peaks as shown by the fact that the peak of 7Si1Ge appears at larger ppm than that of 8Ge. Further, the absolute value of 5 ppm for 7Si1Ge is very far from the experimental −20 ppm. 'Model A' only shows a good agreement for the '8Si' peak which appears at −43.3 ppm, close to the experimental value −38 ppm, showing that the F^- assignment in the centre of the D4R-8Si is correct.

The results from 'Model B' (Fig. 1c) reproduce the relative order of the three signals corresponding to 8Si, 7Si1Ge and 8Ge, and the calculated values are −43.3, −33.3 and −28.8 ppm respectively, in reasonable agreement with the experimental values. In order to test whether these results are biased by the basis set used, two more basis sets have been used and the results (see Table 1) show that the relative trends are kept.

First principles simulations of NMR chemical shifts have been previously performed on zeolites but this is, to the best of our knowledge, the first computational study of ^{19}F NMR chemical shifts in zeolites. It is shown that, unlike in the case of F-D4R-8Si where silicon is tetracoordinated, germanium forms a covalent bond with the occluded fluoride giving a pentacoordinated germanium in the D4R. The implications of these results in the synthesis of Si/Ge zeolites are that D4R units in the presence of fluoride anions are formed more easily with germanium than with silicon because of the larger stability of the covalent Ge–F bond with respect to the ionic Si···F interaction.

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