

## Dynamic anions in small cages

### Dynamics of fluoride anions in all-silica and silicogermanate zeolites

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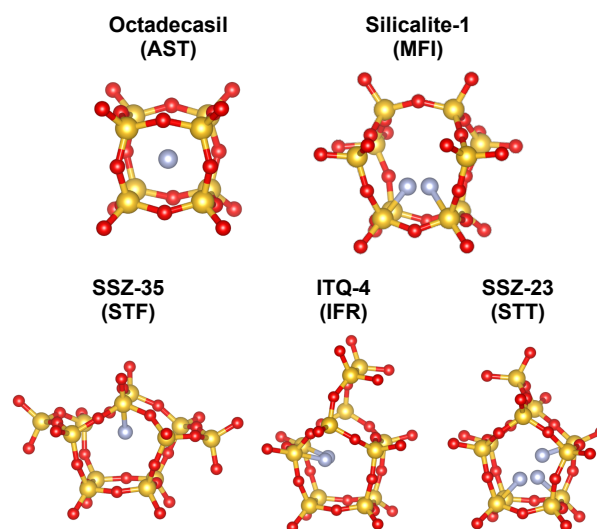
#### In Short

- *ab-initio* molecular dynamics calculations are used to study the dynamic behaviour of fluoride anions confined to small cages in zeolite structures.
- The local environment and dynamic behaviour of fluoride anions in AST-type zeotypes having different composition has been investigated.
- The influence of the organic cation on the dynamic disorder of fluoride anions in MFI-type Silicalite-1 has been elucidated.
- Ongoing work compares all-silica zeolites with various topologies in order to study the impact of different factors on the dynamic disorder.

Zeolites are a class of inorganic porous materials with important applications in ion exchange, gas and liquid separation, and catalysis.[1] Zeolite structures consist of a three-dimensional framework of tetrahedrally coordinated T atoms connected by oxygen atoms. Prototypical zeolites, such as zeolite minerals, possess a negatively charged aluminosilicate framework whose charge is balanced by extra-framework cations. The development of sophisticated synthesis routes has led to the discovery of zeolite-like materials having a neutral framework, among them all-silica zeolites (composition  $\text{SiO}_2$ ), germanates ( $\text{GeO}_2$ ), silicogermanates ( $\text{Si}_x\text{Ge}_{1-x}\text{O}_2$ ), aluminophosphates ( $\text{AlPO}_4$ ), and gallophosphates ( $\text{GaPO}_4$ ). The synthesis in the presence of fluoride anions is a particularly successful strategy to obtain neutral-framework zeotypes with very open frameworks and low defect concentrations. Various zeolites and zeotypes with unprecedented framework topologies can be synthesised via this route, many of which have (so far) not been obtained in the absence of fluoride.[2,3]

In the as-synthesised zeolites, the fluoride anions occupy well-defined positions in the crystal structure, balancing the charge of the organic cations used to direct the formation of a particular structure (organic structure-directing agent = OSDA). In zeolites having double four-ring (*d4r*) cages, the fluoride anions occupy the centre of this cage (shown for octadecasil in Figure 1). In one part of this project, *ab-initio* molecular dynamics (AIMD) calculations based on density-functional theory (DFT) were used to study

the local environment and the dynamic behaviour of fluoride anions in zeolites containing *d4r* cages, focussing on the AST framework type as a prototypical example. Such an AIMD approach allows to obtain a first-principles perspective of the zeolite's dynamic behaviour on the timescale of picoseconds. A comprehensive AIMD study investigated the local environment and dynamic behaviour of fluoride anions confined to *d4r* cages of AST-type silicogermanates, revealing a pronounced dependence of the equilibrium position of fluoride, and its dynamic behaviour, on the distribution of Si and Ge on the corners of the cages.[4] This work was subsequently extended to include AST-type systems having alumino- and gallophosphate compositions. In these zeotypes, the fluoride anions tend to form short-lived bonds to the Al/Ga atoms, jumping between different positions on the picosecond timescale (at room temperature). As a consequence, diffraction methods, which probe a much longer timescale, locate the fluoride anions closer to the cage centre.[3]



**Figure 1:** Visualisation of fluoride environments in different zeolites. Framework type codes are given in brackets. Among the systems in the lower part, ITQ-4 and SSZ-23 show dynamic disorder of the fluoride anions, whereas SSZ-35 exhibits no dynamic disorder.

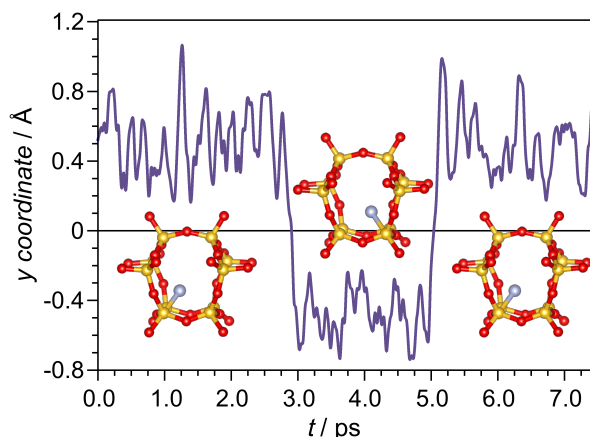
In structures without *d4r* units, fluoride anions also tend to occupy small cages. However, rather than being located at the cage centre, they are covalently bonded to a single silicon atom, forming trigonal-bipyramidal  $\text{SiO}_4\text{F}^-$  units. Frequently, the fluoride anions are disordered over two or more positions within one cage, as shown for several all-silica zeolites in Figure 1. Among these systems, Silicalite-1, ITQ-4,

and SSZ-23 exhibit dynamic disorder of the fluoride anions at room temperature.[5] This means that the anions "jump" between different positions on a very short timescale that is accessible with nuclear magnetic resonance (NMR) experiments. Upon cooling to cryogenic temperatures, characteristic changes in the NMR spectra show that the dynamic motion is frozen out. Moreover, the extent of the dynamic disorder at room temperature depends on the organic cation.[6]

MFI-type zeolites are particularly interesting due to their large relevance for applications (catalysis, separation). DFT-based AIMD calculations for Silicalite-1 incorporating tetrapropylammonium (TPA<sup>+</sup>) cations revealed that the dynamic disorder of the fluoride anions at room temperature is difficult to resolve due to the short timescale that is accessible with the computations. However, an increase of the simulation temperature to 100 or 200 °C permitted a semi-quantitative analysis, allowing the determination of the number of "hopping events" happening during a given simulation time (as illustrated in Figure 2; a hopping event corresponds to a discontinuous change in the fluoride position, where the anion moves from one Si atom to an adjacent one). A comparison of Silicalite-1 models incorporating different OSDAs showed a drastic reduction in the number of hopping events in those systems where the OSDA has one short (methyl or ethyl) and three long (butyl) chains, in agreement with experimental observations.[6] An atomic-level explanation for the influence of the OSDA on the fluoride dynamics was developed by considering both the charge distribution and the motional freedom of the organic species.[7] Future work on MFI-type systems will compare systems with ammonium-based OSDAs to those containing phosphonium or arsonium cations.

Ongoing calculations compare a total of six all-silica zeolites with SiO<sub>4</sub>F<sup>-</sup> units for which a significant variation of the dynamic disorder at room temperature has been found experimentally. Among the three systems illustrated in the lower part of Figure 1, dynamic disorder occurs in ITQ-4 and SSZ-23, but not in SSZ-35, despite the similar local environment.[5,8] As for MFI, these observations can be reproduced in the AIMD simulations, at least on a qualitative level, when increasing the simulation temperature to 100 or 200 °C. The further analysis of the results will aim to establish whether the local environment within the cage, the interaction of fluoride anions and OSDA cations, or a combination of both factors determine the dynamic behaviour.

Future calculations are planned for ZSM-50, which can be synthesised using a complex fluoride-containing OSDA, and for ITQ-13, a zeolite in which both fluoride environments (*d4r* cages and SiO<sub>4</sub>F<sup>-</sup> units) coexist.



**Figure 2:** Evolution of the y coordinate of a fluoride anion over the course of a 7.5 ps trajectory (example: TPA<sup>+</sup>-containing MFI at 100 °C). The discontinuities after about 3 and 5 ps correspond to "hopping events". The approximate average positions of fluoride are illustrated in the insets.

## WWW

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## More Information

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