

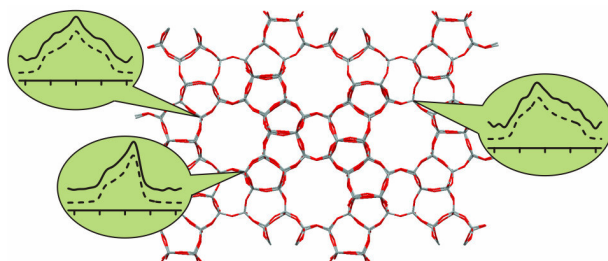
## Refinement of zeolite crystal structures using ultrahigh-field measurements and *ab initio* calculations of $^{29}\text{Si}$ chemical shift tensors

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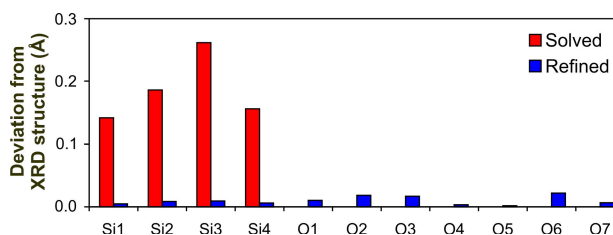
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The principal components of zeolite  $^{29}\text{Si}$  chemical shift tensors have recently been accurately measured and calculated for the first time [1]. The experiments were performed at an ultrahigh magnetic field of 21.1 T in order to observe the small anisotropies of the  $^{29}\text{Si}$  shielding interactions that arise for Si atoms in near-tetrahedral geometries (Figure 1). The  $^{29}\text{Si}$  shielding tensors calculated using Hartree-Fock *ab initio* calculations on clusters derived from the crystal structures are in excellent agreement with the experimental results. The accuracy of the calculations is strongly dependent on the quality of the crystal structure used, indicating that the  $^{29}\text{Si}$  shielding interaction is extremely sensitive to the local structure around each Si atom. These NMR measurements and calculations have been incorporated into a structure refinement method [2,3] that complements the recently described structure solution method from  $^{29}\text{Si}$  double-quantum NMR data [4], providing a near-complete suite of tools for the NMR crystallography of zeolites. For the zeolite Sigma-2, the NMR solved and refined crystal structure [2] was found to be virtually indistinguishable from the single-crystal X-ray diffraction crystal structure (Figure 2). The NMR structure refinement strategy was also applied to the zeolite ZSM-12 and yielded an improved crystal structure over the previous powder XRD structure [3].



**Figure 1:**  $^{29}\text{Si}$  quasi-static powder patterns for Si sites in the zeolite ZSM-5.



**Figure 2:** Deviations of the NMR-determined atomic coordinates from the single-crystal XRD structure for the zeolite Sigma-2.

### References

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- [3] D.H. Brouwer, Crystal structure refinement with solid-state NMR: An improved structure of silica-ZSM-12 zeolite from  $^{29}\text{Si}$  chemical shift tensors, *J. Magn. Reson.* **194** (2008) 136-146.
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