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Computer modeling of apparently straight bond angles: The intriguing case of all-silica ferrierite

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Abstract

The relationships between synthetic zeolites and their natural counterparts that have been unveiled by theoretical studies have contributed to improving the properties and applications of zeolite-based materials in strategic areas such as industrial catalysis, environmental protection, and solar energy harvesting. To pinpoint the role of modeling in zeolite science, we discuss an example of computationally driven problem solving: can tetrahedral frameworks sustain straight (i.e., 180°) Si-O-Si bond angles? The true crystal symmetry of zeolite ferrierite (FER), especially in its all-silica form, had been intensely debated for 30 years before being solved in the *Pmnn* space group. Yet there are indications that an *Immm* structure with energetically unfavorable linear Si-O-Si linkages could be formed at high temperature. To gather insight, we perform density functional theory (DFT) optimizations and frequency calculations of all-silica ferrierite in both the *Pmnn* and *Immm* space groups. Our results indicate that *Pmnn* is more stable than *Immm*, in line with experiments. While the *Pmnn* structure is a true minimum in the energy profile of ferrierite, the *Immm* structure has four imaginary frequency vibrations, three of which are localized on the 180° Si-O-Si angles. This suggests that ferrierites with *Immm* symmetry may be classified as metastable phases. Such a designation is also supported by first-principles molecular dynamics on *Immm* FER, showing that the average value of 180° actually results from Si-O-Si angle inversion. An implication of this study with interesting geological and technological consequences is the association of straight Si-O-Si angles experimentally detected in open-framework or low-density silicates to an angle-inversion process occurring at the femtosecond scale. Such flexibility of the apparently flat Si-O-Si linkages might play an important role in sorption phenomena, which are ubiquitous in geological processes and industrial applications alike.

Keywords: Zeolites, high temperature, framework flexibility, open framework silicates, molecular dynamics, density functional theory; Microporous Materials: Crystal-Chemistry, Properties, and Utilizations