The influence of the long-range order on the vibrational spectra of structures based on sodalite cage

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HIGHLIGHTS

- Theoretical spectra of optimized cluster and periodic models were calculated.
- IR and Raman spectroscopy were used to obtain experimental spectra of sodalite and LTA.
- Based on the comparison of theoretical and experimental data bands were identified.
- The influence of the long-range interactions on the vibrational spectra were assessed.
- The description of experimental FIR spectra is possible based on the periodic models.

GRAPHICAL ABSTRACT
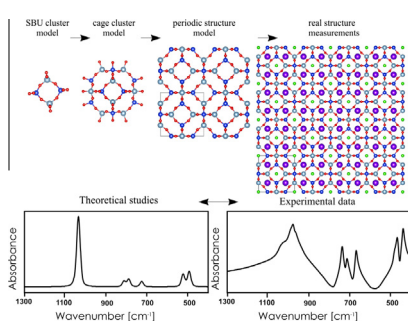
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ABSTRACT

Zeolites are a group of tecto-aluminosilicates with numerous practical applications, e.g. gas separators, molecular sieves and sorbents. The unique properties result from porous structure of channels and cages which are built from smaller units – the so-called *Secondary Building Units* (*SBU*), and sometimes also larger groups (Breck, 1974; Ciciszwili et al., 1974; Mozgawa, 2008; Čejka and van Bekkum, 2005).

The aim of this study was the examination of the influence of long-range order on vibrational spectra of sodalite and zeolite A. *Ab initio* calculations (geometry optimizations and vibrational spectra calculations) of sodalite cage and selected *SBU* were carried out by means of *Gaussian09* (Frisch et al., 2009) (in the case of isolated clusters) and *Crystal09* (Dovesi et al., 2005, 2009) (for periodic structures). The obtained results were compared with the experimental spectra of sodalite and zeolite A crystal structures, synthesized under hydrothermal conditions. These results allowed analyzing of the long-range ordering influence on the vibrational spectra, as well as the identification of the characteristic vibrations in β cage based frameworks.

It has been found, that based on small structural fragment (*SBU*) models a characteristic vibrations can be identify. However, full spectra analysis and especially the interpretation of far-infrared region of the spectra require using periodic models under the influence of translational crystal lattice.

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Introduction

Zeolites are one of the most intensively studied groups of materials in recent years. Gas separators, molecular sieves, nanomedicine, ion exchangers, sorbents, and above all, catalysis are the

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main examples of their uses [1–3]. Such wide range of applications results from the unique zeolite properties, which are direct consequence of their specific structure.

Zeolites are hydrated tecto-aluminosilicates with a microporous (or mesoporous) system of channels and cages of strictly defined sizes and geometries. Those systems are built from smaller units, the so-called *Secondary Building Units* (*SBU*), which are the foundation of their systematics [1,4,5]. In some cases, it is even possible to specify larger units, which can be found in various zeolite frameworks, such as sodalite cage (*β* cage) (Fig. 1) [6,7]. A number of possible connections between both, *SBU* and larger units in zeolite structures is very large, which results in a huge variety of zeolite forms. This variety, as well as specific properties related to particular zeolite structure such as: strictly defined pore sizes and shapes, the possibility of substitution of silicon/aluminium in a framework and hence ion exchange selectivity, presence of catalytic centers *etc.* result in much attention and intensive studies of this group of materials.

Their extensive experimental studies are often supported by theoretical considerations, based on a group of *ab initio* computational methods [3,4]. Such calculations, when compared with the results of spectroscopic measurements, can be a valuable source of information about selected structural properties. This is particularly noticeable in the published works regarding to the catalytic and ion exchange properties of zeolites [4,8–12]. Most of these papers, however, focus on modeling of selected, small structural fragments. Such approach is due to several reasons. First, in the case of catalytic properties, important studies are devoted to chosen structure elements which can serve as potential acidic centers, as well as to their interactions with chosen molecules. In this case, calculations carried out for small clusters are usually sufficient and sometimes complemented by the so-called hybrid computational techniques (*e.g.* ONIOM method) [3]. Second, in other studies (primarily related to the interpretation of vibrational spectra and other structural properties of whole systems), the crucial problem pose the complexity of zeolites structures. Unit cells of these aluminosilicates may consist of up to several thousands of atoms, which significantly limits the use of *ab initio* methods due to available computing power and calculations time. For these reasons, it was necessary to apply the simplified models and perform calculations for small clusters. Large amount of papers focus on theoretical models of the *SBU* and few larger units, which allowed identification of ring vibrations, assigning fragments of spectra to the various structural groups, *etc.* [4,12,13]. However, such simplified models cannot be used for accurate descriptions of far-infrared part of spectra related to lattice and extra framework cations vibrations.

The aim of this study was to assess the influence of the long-range order on the infrared and Raman spectra of chosen structures based on sodalite cage. The choice of this unit was dictated by several reasons. Sodalite cage (*β* cage) is one of the biggest structure fragment found in zeolite frameworks (Fig. 1), *e.g.* SOD, LTA, FAU, MAR, TSC, LTN [7] (most of them widely used in catalysis and as sorbents or ion exchange materials [1,3]). It consists of eight six-membered (S6R) and six four-membered (S4R) rings, which are essential building blocks of many zeolite frameworks and void inside this cage allows hosting most of the cations and even some molecules.
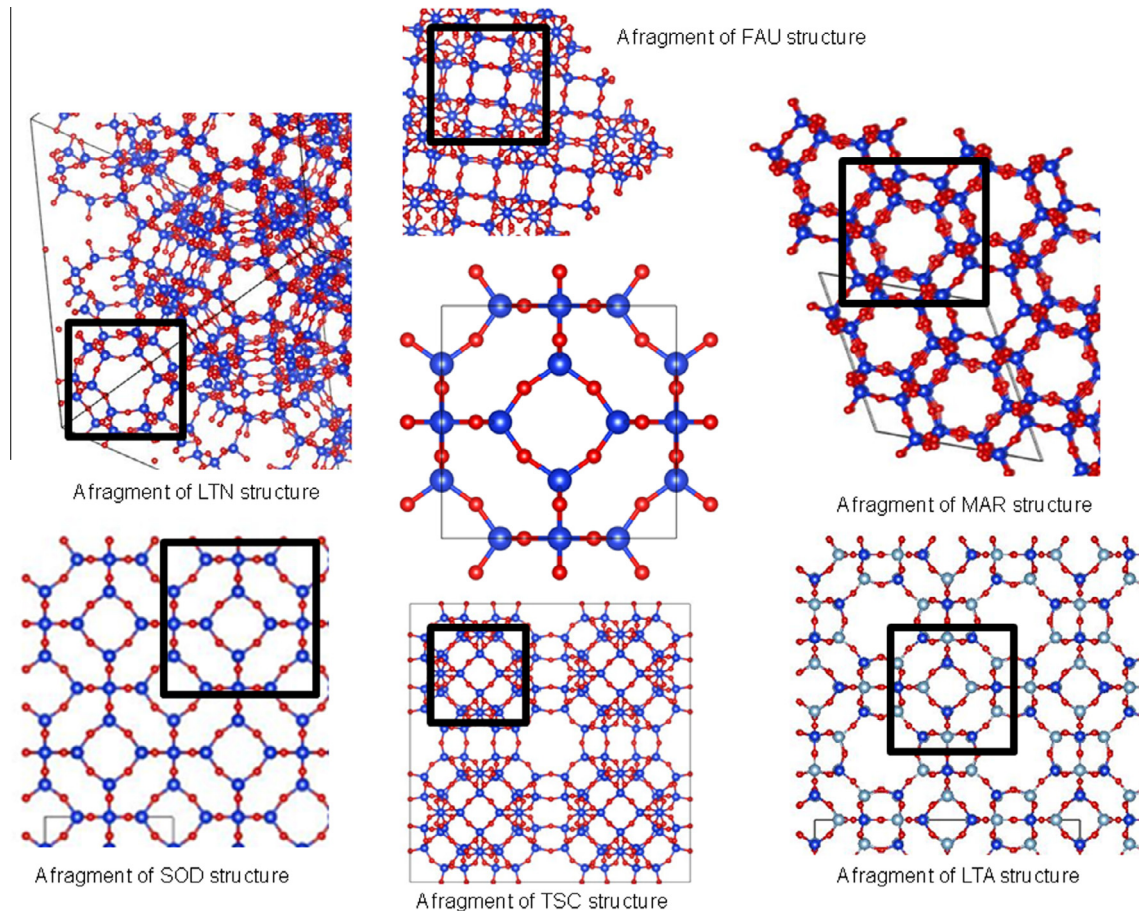

Fig. 1. Sodalite cage in different fragments of zeolite frameworks.