

# Vibrational dynamics of small molecules adsorbed in confined space of zeolite channels

*P. Nachtigall*

*Center for Biomolecules and Complex Molecular Systems, Institute of Organic Chemistry and Biochemistry, Flemingovo n. 2, 166 10 Prague 6, Czech Republic*

Knowledge of the localization and coordination of extraframework cations in zeolites is important for understanding their sorption properties (gas separation, gas storage) and catalytic activity. The extraframework cations are localized in the vicinity of framework aluminum, thus, the knowledge of cation localization bears some information about the framework Al distribution. Due to the limitations of experimental methods, the information about the metal coordination and localization in high-silica zeolites are often investigated by indirect spectroscopic techniques, including spectroscopic characterization of adsorbed probe molecules. Due to a high sensitivity of CO stretching vibrations on its environment the carbon monoxide is the most extensively used probe in IR spectroscopy. IR spectra of CO adsorbed on various alkali metal cations in various zeolites appear to be rather different. They differ in number of distinguishable bands and in the spectra dependence on the CO coverage. Despite a large number of experimental studies the individual features in spectra are not understood and interpreted at the atomic scale level. Therefore, the question of site-specificity of IR spectra of adsorbed CO molecule on metal ion exchanged zeolites is widely discussed in the literature. Extraframework alkali metal cations in zeolite were often studied theoretically, however, in majority of cases the small cluster models were used and only one type of cation coordination (corresponding to one particular site in zeolite) was investigated.

In the present study we systematically investigate the alkali metal cation sites in high-silica zeolites (FER and MFI) and the interaction of CO (formation of mono- and di-carbonyl complexes) with  $M^+$  sites in zeolites using periodic DFT model and  $\nu_{CO}-r_{CO}$  scaling. Theoretical results are compared with experimental data obtained for FER and MFI zeolites with various Si/Al ratios.

Theoretical and experimental results can be summarized as follows:

- (i) Vibrational frequencies of CO adsorbed in alkali metal exchanged zeolites can be calculated with near-spectroscopic accuracy; calculated and experimental frequencies are in excellent agreement. Based on such a good agreement between theory and experiment the individual spectral characteristics can be interpreted at the atomic scale level.
- (ii) The CO vibrational frequency depends primarily on the metal/framework coordination that, in turn, depends on the metal cation size and framework topology. In addition, the CO frequency depends on the number of framework Al in the vicinity of metal cation, on the size of the zeolite channel/cavity where CO is located, and on the presence of second extraframework cation in the vicinity of CO.
- (iii) The information about the metal cation coordination with the framework can be obtained from the comparison of experimental and theoretical spectra: small  $Li^+$  cations preferably coordinates on top of the five- or six-member ring while the larger  $K^+$  ions are preferably located at the channel intersection or they fit well in the eight-member ring of the zeolite structure.