

## **A theoretical study of structural factors correlated with $^{23}\text{Na}$ NMR parameters**

**YUN LIU,<sup>1,\*</sup> JOHN TOSSELL,<sup>1</sup> AND HANNA NEKVASIL<sup>2</sup>**

<sup>1</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, U.S.A.

<sup>2</sup>Department of Geosciences, State University of New York at Stony Brook, New York 11794-2100, U.S.A.

### **ABSTRACT**

Ab initio NMR calculations at the Hartree-Fock GIAO level with 6-311+G(2df,p) basis sets have been performed on many Na-centered clusters with different O-ligands. Several structural factors that can affect the  $^{23}\text{Na}$  NMR parameters have been carefully investigated. The accuracy of our calculations is checked by comparing calculated  $^{23}\text{Na}$  NMR shieldings for crystalline materials with experimental results. The largest Na-O-ligand distance that contributes to the *deshielding* of the Na atom (i.e., the reduction of the Na shielding from its free ion value) is found to be about 3.5 Å. Quantitative contributions to the Na deshielding from different types of O-ligands are emphasized. These contributions are carefully compared to establish the order of decreasing deshielding as:

OH, NBO(Al) > Al-O-Si > NBO(Si) > Al-OH > H<sub>2</sub>O > Si-O-Si > Si-OH

Based on these results we find there is no single formula that is useful for relating sodium NMR shifts to structural parameters. Na-clustering effects from other nearby cations are also found to tremendously increase the shielding of Na. Finally, the relationships established between local structure and O-ligand identity and the  $^{23}\text{Na}$  NMR shieldings have been used to explain the Na NMR data for hydrous albite glasses.