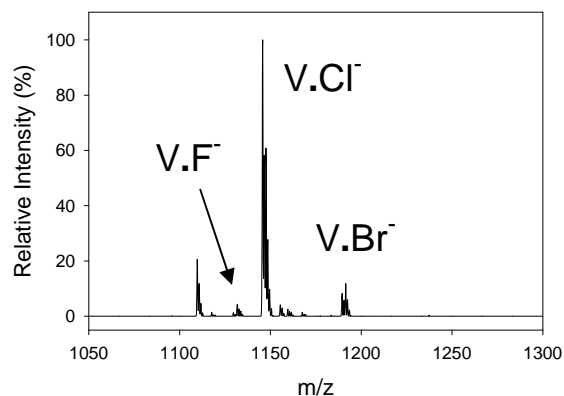


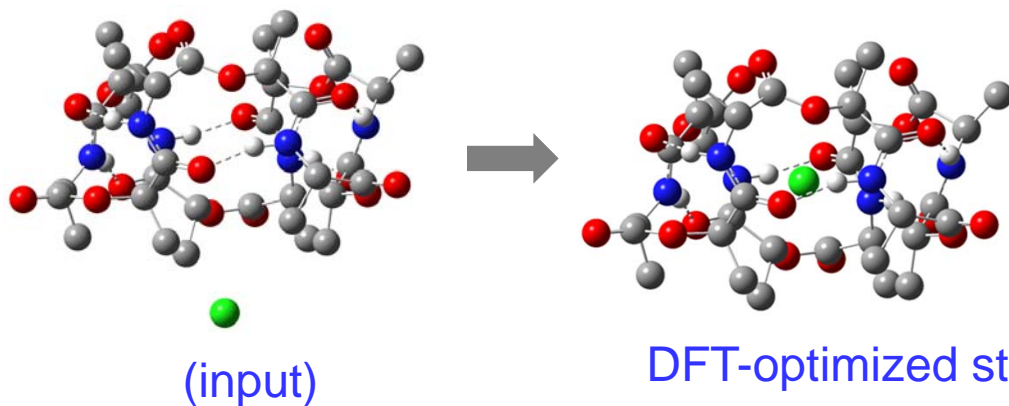
Direct binding of halide ions by valinomycin via ESI-MS, NMR and DFT

Farooq A. Khan, Department of Chemistry, University of West Georgia



ESI mass spectrum of valinomycin (0.010 mM) in the presence of TBAF (0.010 mM), TBACl (0.010 mM), TBABr (0.010 mM) and TBAI (0.010 mM) in methanol. The peaks correspond to the 1:1 adducts formed for halide ions with valinomycin, abbreviated as V.

We report for the first time the binding of valinomycin with anions. The binding selectivity for halide ions for valinomycin is found to be in the order $\text{Cl}^- > \text{Br}^- \sim \text{F}^- \gg \text{I}^-$ based on ESI-MS experiments in methanol. ^1H NMR studies in acetone- d_6 and CD_3CN reveal the binding selectivity of $\text{Cl}^- > \text{Br}^- \gg \text{F}^- \sim \text{I}^-$. NMR studies and DFT calculations support a bracelet-like structure for the binding of a chloride ion to valinomycin. Association constants of 531 ± 45 and $57 \pm 2 \text{ M}^{-1}$ were obtained via NMR titrations in acetone- d_6 for chloride and bromide ions, respectively.



These studies, conducted in collaboration with undergraduate students, Professors Fujita (Chemistry) and Swamy-Mruthinti (Biology) were published in *Supramolecular Chemistry*.