UNRAVELING THE ROLES OF HYDROGEN BONDING, ELECTROSTATICS, AND FERMI RESONANCES IN THE IONIC LIQUID $[\mathrm{EMIM}][\mathrm{BF}_4]$ THROUGH CRYOGENIC ION VIBRATIONAL SPECTROSCOPY

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The importance of hydrogen bonding in imidazolium-based ionic liquids (IL) has become a topic of vigorous debate. Red shifted features in the ring CH stretching region observed in bulk FTIR of several IL have been identified as the hydrogen bonded $C_{(2)}H$ stretch. However, recent theoretical analysis suggests that the complexity of the ring CH stretching region is a result of Fermi resonance interactions between the overtones and combination bands of the ring stretching modes with the ring CH stretches. To help clarify the role of the $C_{(2)}H$ group and the nature of the intermolecular cation-anion interactions, we report the vibrational spectra of cryogenically cooled, composition-selected ionic clusters of the prototypical IL $[\mathrm{EMIM}][\mathrm{BF}_4]$. We have confirmed that the CH stretching region is indeed plagued by strong Fermi resonance interactions and, therefore, have turned to isotopic and chemical substitution to determine the position and role of the $C_{(2)}H$ oscillator. The spectra are consistent with electrostatics being the dominant interaction while hydrogen bonding is not critical in this IL.

Time permitting, recent spectra on temperature controlled protonated water clusters will be discussed.