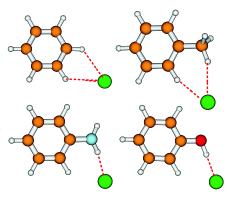
## ARGON PREDISSOCIATION SPECTROSCOPY OF $Cl^-C_6H_5X$ . Ar (X = H, CH<sub>3</sub>, NH<sub>2</sub> and OH) CLUSTERS

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Infrared spectra in the 2500-3700 cm<sup>-1</sup> region have been measured for the chloride anion bound to a number of different aromatic species [Cl<sup>-</sup>-C<sub>6</sub>H<sub>5</sub>X.Ar (X = H, CH<sub>3</sub>, NH<sub>2</sub> and OH)]. The vibrational predissociation spectra were measured using a tandem mass spectrometer. All four species are limited in their ability to dissociate since the binding energy of the anion is less than the energy imparted by the infrared photon exciting the CH stretch region. In cases where  $D_0 \simeq h\nu$ , spectra are likely to exhibit significant hot band contributions, and where  $D_0 \gg h\nu$ , clusters are not likely to dissociate at all. These conditions neccessitate the use of argon predissociation spectroscopy whereby an argonbound cluster is selected with subsequent dissociation of the rare gas upon absorption of an infrared photon. The heat of association for the bound argon is significantly less than even the most weakly bound of these four clusters - (D<sub>0</sub>(Cl<sup>-</sup> Ar) = 523 cm<sup>-1</sup> compared to D<sub>0</sub>(Cl<sup>-</sup>(Bz)) = 3288cm<sup>-1</sup>). As an additional benefit of using this method, the internal energy of the complexes formed in our supersonic expansion are limited by the argon as-



sociation energy and thus yield cooler clusters. Comparison with earlier argonless spectra illustrates the cooling effect with significantly reduced linewidths and fewer features, allowing assignments previously in dispute to be confidently assigned to hot bands. Importantly, the comparison also confirms that the perturbing effect of a bound argon is negligible. The interpretation of spectra is assisted through 2nd order Moller-Plessett theory *ab initio* calculations. Particularly in the case of both  $Cl^- - C_6H_6$  and  $Cl^- - C_6H_5CH_3$ , relative energies and harmonic frequency calculations for different conformations enable confident assignments to be made.