Denver

CHEMISTRY

Fall 2023
SEMINAR SERIES

11am – noon
Oct. 20th
NC 1130

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Halogen bonding and other σ-Hole Interactions Revisited After 18 Years

A covalently-bonded atom typically has a region of lower electronic density, a "σ-hole," on the side of the atom opposite to the bond, along its extension. There is frequently a positive electrostatic potential associated with this region, through which the atom can interact attractively but noncovalently with negative sites. This was first pointed out in the 2005 for covalently-bonded halogens and was then extended to other main group elements in 2007 – 2009. This positive potential reflects not only the lower electronic density of the σ-hole but also contributions from other portions of the molecule. These can significantly influence both the value and also the angular position of the positive potential, causing it to deviate from the extension of the covalent bond. We have surveyed these effects, and their consequences for the directionalities of subsequent noncovalent intermolecular interactions, for atoms of Groups IV-VII. The overall trends are that larger deviations of the positive potential result in less linear intermolecular interactions, while smaller deviations lead to more linear interactions. We find that the deviations of the positive potentials and the nonlinearities of the noncovalent interactions tend to be greatest for atoms of Groups V and VI. These "σ-hole" interactions have in the past few years been extended to the transition metals and also the noble gases.