Spectroscopy and Dynamics of the Bond, Inter- and Intra Molecular!

Arijit Das, Sharon Priya Gnanasekar, and Elangannan Arunan
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India
E-mail: arunan@iisc.ac.in

Abstract

In 2009, Goswami and Arunan proposed a condition for hydrogen bonding according to which there should at least be one bound-level along vibrational coordinates which lead to breaking of the hydrogen bond.[1] They showed that this is the significant difference between the open tetrahedron structure of ice and the close packed structure of solid H2S, and they are not the results of the difference between ‘hydrogen bonding’ and ‘van der Waals interactions’ as commonly assumed. When it comes to the dimers of H2O and H2S, there were plenty of experimental and theoretical results available for the former and very little for the latter. Recently, our group in collaboration with Newcastle University, UK and the National Institute of Standards and Technology, U.S.A. have observed the K=1 transitions of H2S dimer which unambiguously showed that H2S dimer is hydrogen bonded.[2]. We have now calculated the barriers along the various large amplitude motions in H2S dimer and shown that it indeed satisfies the criterion of Goswami and Arunan.

Following the popular characterization of CH5+ as a 3c-2e bond between the CH3 tripod and H2 moiety,[3] we explored the bonding of protonated methane/silane/germane. Our objective was to understand whether the 3c-2e bond was ‘V’ shaped or ‘T’ shaped, as in the latter case it could resemble a ‘carbon (tetrel) bond’[4] between H2 and C+. This investigation led to intriguing findings [5] about CH5+, SiH5+ and GeH5+ and also the ill-defined 3c-2e bonds, see Figure 1. Proton adds to C in CH4 forming five C-H bonds and H in SiH4/GeH4, forming a H2 tetrel bonded to SiH3+/GeH3+. The talk will highlight our recent results on the intermolecular bonding in HSS dimer and the intramolecular bonding in TH5+ (T = C/Si/Ge, a tetrel atom). Following these results, we could categorize six three-centre-two-electron bonds, based on the electron density topology into six categories: V, T, L, I, Y and \( \Delta \).

Fig. 1: Molecular graphs for the TH5+ molecule calculated at MP2/aug-cc-pVTZ.

Keywords: Hydrogen bond, microwave spectroscopy, three-centre-two-electron bond, carbon/tetrel bond, Atoms in Molecules Theory

References: