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2020

Das, A., Gnanasekar, S. P., & Arunan, E. (2020). Spectroscopy and dynamics of the bond, inter- and intra molecular!. Proceedings of the 7th Asian Spectroscopy Conference 2020 (ASC 2020). doi:10.32655/ASC_8-10_Dec2020.2

<https://hdl.handle.net/10356/143538>

https://doi.org/10.32655/ASC_8-10_Dec2020.2

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

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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 H₂S dimer and the intramolecular bonding in TH₅⁺ (T = C/Si/Ge, a tetrel atom). Following these results, we could categorize⁶ three-centre-two-electron bonds, based on the electron density topology into six categories: V, T, L, I, Y and Δ.

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:

- [1] M. Goswami and E. Arunan, *Phys. Chem. Chem. Phys.*, **2009**, *11*, 8974.
- [2] A. Das, P. K. Mandal, F. J. Lovas, C. Medcraft, N. R. Walker and E. Arunan, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 15199.
- [3] D. Marx and M. Parrinello, *Nature*, **1995**, *375*, 216 and many other papers on CH₅⁺.
- [4] D. Mani and E. Arunan, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 14377.
- [5] S. P. Gnanasekar and E. Arunan, *J. Phys. Chem. A*, **2019**, *123*, 1168 (Featured as a cover article).
- [6] S. P. Gnanasekar and E. Arunan, *Aust. J. Chem.* **2020**, <https://doi.org/10.1071/CH19557>.