

# Nature and Strength of Unconventional Hydrogen Bonds

PT9.

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Intermolecular interaction involving hydrides of the most electronegative elements such O, N, halogens and electron rich atoms or group of atoms of neighboring molecules has been termed and widely accepted as hydrogen bonding interaction. In the traditional definition of the conventional H-bond the most highlighted part is that in the  $XH\cdots Y$  type of interactions both X and Y must be highly electronegative. There had been, however, reluctance to accept the interactions involving hydrides of lesser electronegative elements such as carbon, sulfur, selenium as H-bonding interactions. In early days classifying such interactions as H-bonding was based on the bond distance criteria obtained from the crystallographic database, and to a limited extent on the NMR and IR data due to lack of any other spectroscopic data and was heavily contested at times. The most celebrated case has been the CH-Y interaction.

In the last couple of decades a significant progress has been made in regard to obtaining the spectroscopic data on weak hydrogen bonding interactions in an isolated condition of gas phase. Our group has been working on characterization of several unconventional hydrogen bonds. The adjective *unconventional* is used to differentiate the  $XH\cdots Y$  hydrogen bonds that do not involve strongly electronegative X or Y atoms or group of atoms. The emphasis has been on the sulfur centered hydrogen bonds and  $CH\cdots Y$  type hydrogen bonds. In this talk I will present our spectroscopic results on the selected examples of both types. We show that the sulfur centered H-bonding interaction is dominated by the dispersion interaction besides showing all the characteristics of conventional hydrogen bond. In the case of  $CH\cdots Y$  type hydrogen bonds I will show examples of red, blue, and zero shift hydrogen bonds. I will also show that the  $CH\cdots Y$  hydrogen bonds also exhibit all the characteristics of conventional proper hydrogen bonds and there is nothing improper about it.

# High resolution spectra of floppy molecules: neutral and ionic species

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Recent progress in the experimental technique in spectroscopy, i.e. in resolution, precision, and sensitivity, makes it possible to investigate the static and dynamic behavior of molecules in detail. Consequently, or better to say surprisingly, we are facing now a variety of difficulties to explain the observed phenomena due to the large amplitude motions involved. Very often, they are not easy to be handled by the standard theory which have been developed with the assumptions of small amplitude vibration.

In this lecture several results for HOOD [1],  $C_3$  [2], and  $CH_5^+$  [3] will be presented, as well as some newly investigated ionic species. The spectra of neutral species have been observed and analyzed recently by the spectroscopy group of Kassel university, and those of ionic species by the group of Cologne University.

Hydrogen peroxide is a classical example of the molecule with a large amplitude motion (i.e. internal rotation or torsion). Although the spectra of HOOH and DOOD have been investigated in detail and we understand the structure including the torsional potential, for the remaining isotopologue, HOOD, details were not known for long years. In the last decade we have measured and assigned the FIR and THz spectra in Kassel [1]. In the study we found accidental resonances between the tunnel doublets in the lowest  $K_a$  levels, which blocked the assignment for long years.

The  $C_3$  radical is also known as a molecule with a large amplitude motion. Recently the THz spectra of the bending fundamental ( $\nu_2$ ) band was successfully measured and analyzed in Kassel [2]. In the course of structure determination, we found that the moment of inertia along the molecular axis  $I_z$  may not be zero in average in the ground vibrational state although it should vanish in the  $r_e$  structure.

High resolution IR and THz spectroscopy of ions trapped in a cryogenic ion trap has been developed by Schlemmer and coworkers in Cologne. By using the trap, they have been very successful in observing numerous ionic species, of rigid or non-rigid structure. The awfully complicated spectra of  $CH_5^+$  were measured in IR and we have published a paper in 2015 [3], where several combination differences for the ground vibrational state are reported, without proper assignments.

It would need still many years, or decades, to tame these *enfant terribles* in spectroscopy including the  $CH_5^+$  ion.

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