Investigating the characteristics of hydrogen bonding between chalcogen and pnictogen species

Graneri, M.H.V.G.,* Wild, D.A., McKinley, A.J.
University of Western Australia, Australia
*matthew.graneri@research.uwa.edu.au

Research into hydrogen bonding has broadly focused on interactions with oxygen-containing species. Complexes with water, methanol, esters, and ketones are very important systems to characterise for a full understanding of both atmospheric and interstellar chemical processes. However, this means that systems of non-oxygenated molecules have received less attention, despite their own importance.

As such, we have conducted matrix isolation Fourier transform infrared (MI-FTIR) spectroscopy experiments looking at the interactions between several molecules of relevance to the atmospheres of Earth and other planets in our solar system. The formation of complexes between H_2S and NH_3, methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA) have been observed experimentally. These experiments have been complemented by high-level ab initio and density functional theory (DFT) calculations which provided quantitative estimates of binding energies, equilibrium structures and vibrational frequencies.

From the results of this work, we believed we could posit a general trend in the binding strength of a molecule to an amine with respect to whether the amine is primary, secondary, or tertiary; however, the relative binding energies we observed showed MA < TMA < DMA, contrary to the expected trend (MA < DMA < TMA), based on gas-phase basicities. Additionally, the spectra of each H_2S•amine complex contain equivalent (but not identical) 'mystery peaks' which we cannot yet explain. Efforts to reconcile these signals are ongoing.