Gas Phase Detection of the NH···P Hydrogen Bond and Importance of Secondary Interactions
Kristian H. Møller, Anne S. Hansen and Henrik G. Kjaergaard
Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø

Gas phase identification of the NH···P hydrogen bond
The gas phase NH···P hydrogen bond was identified in the complex formed between dimethylamine (DMA) and trimethylphosphine (TMP). The bond was identified using Fourier transform infrared spectroscopy (FT-IR) of the NH-stretching vibration, which was found to be redshifted relative to that of the DMA monomer.

Hydrogen bond angle
The hydrogen bond angle of the DMA-TMP complex, \( \theta_{\text{NH···P}} \), was found to be very sensitive to the computational procedure employed in the geometry optimization. B3LYP and M06-2X resulted in the largest and smallest angles, respectively.

Importance of secondary interactions
Natural Bonding Orbital (NBO) analysis showed that the hydrogen bond angle correlated with the contribution from the hydrogen bond to the total interaction energy, \( \%\text{H-bond(NBO)} \). The NBO results also indicated that the large sensitivity to the choice of computational method could be ascribed the relatively large contribution to the total energy from the secondary interactions. The secondary interactions are defined as all inter unit interactions other than the NH···P hydrogen bond.

Confirmed by topological results
The NBO results are supported by results from the topological methods Atoms In Molecules (AIM) and Non-Covalent Interactions (NCI), which also serve to further highlight the differences between the different computational methods.

References