PhLAM RESEARCH SEMINAR SERIES
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« Exploring Molecular Dimerization in the Gas Phase Using Broadband Rotational Spectroscopy: π -Stacking vs Hydrogen Bond. »

By
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This talk will explore molecular dimerization in the gas phase using jet-cooled chirped-pulse rotational spectroscopy. The molecular targets will include mono and biarenes functionalized with a thiol or an alcohol group. This study illustrates the molecular factors balancing □-stacking and hydrogen bonding, typically showing a negative correlation. The smaller monoarene dimers like (thiophenol)$_2$, (phenol)$_2$ and (thiophenol···phenol) display radically different behavior depending on the strength of the hydrogen bond. Specifically, the thiophenol dimer exhibits a weak a S-H···S hydrogen bond and □-stacking, contrasting with the hinged structure of the O-H···O hydrogen bond in (phenol)$_2$ or the partially stacking structure of thiophenol···phenol, stabilized by an O-H···S hydrogen bond. The thiophenol dimer is also notorious because of the presence of internal dynamics and dimerization isomerism. Enlarging the side chain, as in (benzyl mercaptan)$_2$ or (phenethyl mercaptan)$_2$, destroys □-stacking. Conversely, □-stacking is reinforced in the biarenes by the presence of a second aromatic ring. Two isomers were observed for the stacking dimer of (2-naphthalenethiol)$_2$, which lacks a hydrogen bond. However, the heterodimers of (1-naphthalenethiol···1-naphthol) or (2-naphthalenethiol···2-naphthol) display again a partially stacking structure caused by an O-H···S hydrogen bond.

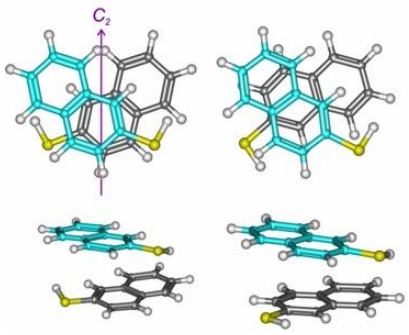

Figure 1. The two observed dimers of (2-naphthalenethiol)$_2$, bound by π -stacking forces.