

## $\pi$ - $\pi$ STACKING IN COMPETITION WITH HYDROGEN BONDING IN THE 1-NAPHTHOL DIMER: A CP-FTMW SPECTROSCOPY STUDY

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Present in a wide spectrum of chemical systems,  $\pi$ - $\pi$  stacking and hydrogen bonding are intermolecular forces critical to the formation and stabilization of various chemical structures. However, these forces can be found to be competitive interactions in stabilizing model systems. This competition is clearly exhibited in the dimer of phenol, where hydrogen bonding is preferred over  $\pi$ - $\pi$  stacking.<sup>a</sup> However, it is unclear how this competitive relationship will evolve as a function of molecular shape. To explore this, we use 1-naphthol, a naphthalene analogue of phenol, as a model to further understand the complex interplay between  $\pi$ - $\pi$  stacking and hydrogen bonding.

Using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 2-6 GHz band<sup>b</sup>, we observed a spectrum that is size-consistent with a dimer of 1-naphthol, in addition to the pure rotational spectra of two conformers of 1-naphthol as well as weakly-bound 1-naphthol complexes with neon and H<sub>2</sub>O. We present an experimental analysis supplemented with a structure search enabled by dispersion corrected DFT and corroborated by interaction energies at the CCSD(T) level of theory, that provides the identity of a likely molecular carrier for the observed dimer spectrum. This analysis suggests that the dimer structure of 1-naphthol is not at all like that of the phenol dimer; conversely, the spectrum is consistent with a structure that stabilizes nearly exclusively through a  $\pi$ - $\pi$  stacking interaction. This is in contradiction to previous observations using IR dip spectroscopy<sup>c</sup>, which assigns the dimer vibrational spectrum to a hydrogen bonded structure.

<sup>a</sup>Seifert, N. A.; Steber, A. L.; Neill, J. L.; Pérez, C.; Zaleski, D. P.; Pate, B. H.; Lesarri, A. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11468–11477.

<sup>b</sup>Pérez, C.; Lobsiger, S.; Seifert, N. A.; Zaleski, D. P.; Temelso, B.; Shields, G. C.; Kisiel, Z.; Pate, B. H. *Chem. Phys. Lett.* **2013**, *571*, 1–15.

<sup>c</sup>Saeki, M.; Ishiuchi, S.; Sakai, M.; Fujii, M. *J. Phys. Chem. A* **2007**, *111*, 1001–1005.