

SMALL NON-COVALENT DIMERS WITH COMPETING HYDROGEN BONDED & HALOGEN BONDED MOTIFS

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The MP2 and CCSD(T) methods have been used in conjunction with large correlation consistent basis sets to characterize simple dimers in which halogen-bonded configurations can be energetically competitive with the hydrogen-bonded structures [1,2]. In the case of dimers formed between HCN and a diatomic hydrogen halide molecule (HX where X = Cl, Br or I), the linear halogen-bonded arrangement (HCN \cdots XH) is a local minimum with an electronic energy that gets closer to that of the corresponding linear hydrogen-bonded global minimum (HCN \cdots HX) as the size of the halogen atom increases. These relative electronic energies decrease from around 4 kcal mol⁻¹ for X = Cl and roughly 3 kcal mol⁻¹ for X = Br to as little as 0.5 kcal mol⁻¹ for X = I near the CCSD(T) complete basis set (CBS) limit. The MP2 and CCSD(T) harmonic vibrational frequencies suggest that it may be feasible to differentiate between these structures spectroscopically. We have also conducted a similar analysis of the dimer formed between HI and acetonitrile (CH₃CN) to investigate the tentative assignment of a second feature in the HI stretching region of the infrared spectrum from matrix isolation experiments to the halogen-bonded configuration. In this system, both the hydrogen-bonded global minimum and the halogen-bonded local minimum have C_{3v} point group symmetry. The latter lies within 1 kcal mol⁻¹ of the former at the CCSD(T) CBS limit, and our harmonic vibrational frequencies corroborate the tentative assignment of that spectral feature in the HI stretching region to the halogen-bonded configuration (CH₃CN \cdots IH). This work on small non-covalent dimers is being extended to azabenzene systems capable of interacting with multiple hydrogen halide molecules (e.g., C₄H₄N₂(HX)₂ and C₃H₃N₃(HX)₃).

[1] Perkins, M.A.; Tschumper, G.S.; Characterization of Competing Halogen- and Hydrogen-Bonding Motifs in Simple Mixed Dimers of HCN and HX (X = F, Cl, Br, and I), *J. Phys. Chem. A*, 2022, **126**, 3688–3695. DOI: 10.1021/acs.jpca.2c02041

[2] Perkins, M.A.; Tschumper, G.S.; Characterization of Competing Halogen-Bonding and Hydrogen-Bonding Motifs in the Acetonitrile/Hydrogen Iodide Dimer, *Chem. Phys.*, 2023, **568**, 111843. DOI: 10.1016/j.chemphys.2023.111843