Abstract Submitted
for the MAR08 Meeting of
The American Physical Society

How Large are Cooperative Effects in Hydrogen Bonded Molecular Chains? MARTIN FUCHS, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin, Germany, JOEL IRETA, Univ. Autonoma Metropolitana Iztapalpa, Mexico — Intermolecular hydrogen bonds play an eminent role in a wide range of materials. In particular, they are critical for the secondary structure stabilization of biopolymers like proteins and nucleic acids. Arrays of hydrogen bonds (hbs), such as in chains or helices, often display a cooperative strengthening of the individual hbs. This cooperativity is crucial for understanding the stability and properties of hydrogen bonded materials. Here we investigate the hb cooperativity in model chains of HCl, HF, HCN, formamide, and 4-pyridone, i.e. molecules forming weak to strong hbs. We calculate the hb strength of infinitely long chains using density-functional theory (DFT) with the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA). We show that for large intermolecular separations, the hbs in the infinite chain strengthen by 20% over the respective molecular dimers, consistent with dipolar electrostatics [1]. At the equilibrium separation, the hbs strengthen significantly further (up to 260% for HF), with additional stabilization from induced dipolar interactions. Comparing with results from higher-level calculations (MP2 and quantum Monte Carlo) we find that DFT faithfully describes the cooperativity in these systems in which the hbs are close to linear. [1] P.B. Allen, J. Chem. Phys. **120**, 2951 (2004)

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Date submitted: 12 Nov 2007 Electronic form version 1.4