

## Accepted Manuscript

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PII: S0009-2614(17)30742-X

DOI: <http://dx.doi.org/10.1016/j.cplett.2017.07.065>

Reference: CPLETT 34991

To appear in: *Chemical Physics Letters*

Received Date: 13 June 2017

Accepted Date: 26 July 2017



Please cite this article as: Y. Tao, W. Zou, E. Kraka, Strengthening of Hydrogen Bonding with the Push-Pull Effect, *Chemical Physics Letters* (2017), doi: <http://dx.doi.org/10.1016/j.cplett.2017.07.065>

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# Strengthening of Hydrogen Bonding with the Push-Pull Effect

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## Abstract

Theoretical studies of hydrogen-bonding based on cluster models tend to overlook the peripheral monomers which are influential. By revisiting thirteen hydrogen-bonded complexes of H<sub>2</sub>O, HF and NH<sub>3</sub>, the “push-pull” effect is identified as a general mechanism that strengthens a hydrogen bond. Enhanced  $Lp(X) \rightarrow \sigma^*(X' - H)$  charge transfer is proved to be the core of the “push-pull” effect. The charge transfer can convert an electrostatic hydrogen bond into a covalent hydrogen bond. †

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## 1. Introduction

Hydrogen bonding (H-bonding) is one of the most important intermolecular forces found in condensed phases, especially in the case of liquid water. It decides on various macroscopic properties including density, boiling point and melting point. In the recent years, various quantum chemical studies attempted to look into the H-bonding by simulating real systems with the help of cluster models consisting of 2 to 20 monomers [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Various computational methods have been used for the analysis of H-bonds including binding energy calculation [1, 6, 7, 8, 10], energy decomposition analyses [12] or the quantum theory of atoms in molecules and the natural bond orbital (NBO) analysis [13]. However, a deeper analysis of how peripheral monomers around a dimer influence the targeted H-bond is often missing.

Experimental studies on the OH stretching frequency shift in small water clusters, supported by DFT calculations, have suggested that the formation and strength of a particular H-bond is influenced by cooperative effects from peripheral H-bonds. [14, 15] However, a caveat is appropriate. Experimentally or theoretically derived normal vibrational modes and force constants are delocalized because of electronic and mass-coupling. [16] Therefore, are not suited

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†In Memoriam of Dieter Cremer

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