

# The Origins of Large Interaction-Induced First Hyperpolarizabilities in Hydrogen-Bonded $\pi$ -Electronic Complexes

Robert W. Góra<sup>1</sup>

<sup>1</sup> Theoretical Chemistry Group, Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Poland

Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, E-mail: robert.gora@pwr.wroc.pl

In this contribution we discuss the origins of interaction-induced linear and non-linear electro-optic properties of model hydrogen-bonded  $\pi$ -electronic complexes. In particular we report on the excess dipole moments ( $\Delta\mu$ ), electric dipole polarizabilities ( $\Delta\alpha$ ) and first hyperpolarizabilities ( $\Delta\beta$ ) – focusing on the latter – of the quasi-linear dimers of urea, diformamide, 4-pyridone, 4-nitroaniline and the complex of hydrogen fluoride with nitroacetylene. The nature of intermolecular interactions as well as of the  $\Delta\mu$  and  $\Delta\alpha$  is very similar in all studied complexes. However, partitioning of  $\Delta\beta$  into physically well defined components (cf. Góra *et al.*[1]) reveals that the origins of this effect, the magnitude of which is often comparable to that of isolated monomers, are different in each case. Interestingly, our results indicate that even though hydrogen bonding usually diminishes the non-linear response of interacting species, the first hyperpolarizability of complexes with nitro group acting as a proton acceptor is substantially increased. On the other hand, the magnitude and sign of interaction-induced first hyperpolarizability depends in some cases strongly on the intermolecular separation which could indicate potentially large vibrational contributions as well as significant sensitivity to external pressure.

[1] Góra, R. W., Zaleśny, R., Zawada, A., Bartkowiak, W., Skwara, B., Papadopoulos, M. G., Silva, D. L. *J. Phys. Chem. A*, 115:4691-4700, 2011.