

Experimental and theoretical evidence of charge transfer in weak H-bonded molecular complexes

¹D.Cappelletti, ²L. Belpassi, ²F. Pirani ²F. Tarantelli

¹*Dipartimento di Ingegneria Civile e Ambientale, Università di Perugia, 06123 Perugia, Italy*

²*Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy*

email: david.cappelletti@unipg.it

We recently [1,2] reported the definitive assessment of a measurable (half a KJ/mol) charge-transfer (CT) component in the interaction of water with the noble gases. By using an original method of partial integration of the change in electron density occurring upon the formation of Ng–water complexes (computed with accurate *ab-initio* methods and basis sets), we map the local charge displacement along the whole intermolecular region and are thus able to appraise CT effects free of the inherent ambiguity of charge decomposition models.

On this line, we extensively explored by molecular beam experiments similar systems such as water-molecule [3], ammonia-rare gas and molecules, hydrogen sulphide-rare gas [4] and molecules, methanol-rare gas and molecules. In this communication, we will mostly focus on the D₂O-D₂ molecular complex [5], but other results will be also reviewed.

The experimental data have been quantitatively analyzed and characterized employing a recently proposed model potential [6] and also exploiting the most recent *ab-initio* PESs [7,8] (including also the deuterated isotopologues) and suggest the presence of a stabilization energy term well beyond the usual van der Waals interaction. An analysis of the electron density displacement shows the CT to be strongly stereo-selective and mediated by a highly asymmetric, donor/acceptor concerted role of the hydrogen atoms on both molecules, which can in fact dictate the equilibrium geometry of the adduct. These findings may be of general relevance in explaining the known peculiar orientational features of water interactions.

- [1] L.Roncaratti, L. Belpassi, et al. *J.Phys. Chem.*, **2009**, *113*, 15223–15232
- [2] L. Belpassi, F. Tarantelli, et al. *Phys. Chem. Chem. Phys.*, **2009**, *11*, 9970–9975.
- [3] D. Cappelletti, P. Candori, et al. *Mol. Phys.*, **2010**, *108*, 2179.
- [4] V. Aquilanti, D. Cappelletti, et al. *Int. J. of Mass Spectrometry* **2009**, *280*, 72–77
- [5] L. Belpassi, M.L. Reca, et al., *J.Am.Chem.Soc.*, *2010*, in press.
- [6] F. Pirani, S. Brizi, et al., *Phys.Chem.Chem.Phys.*, **2008**, *10*, 5489–5503
- [7] M.P. Hodges, R.J. Wheatley et al., *J. Chem. Phys.*, **2004**, *120*, 710.
- [8] P. Valiron et al. , *J.Chem. Phys.*, **2008**, *129*, 134306.