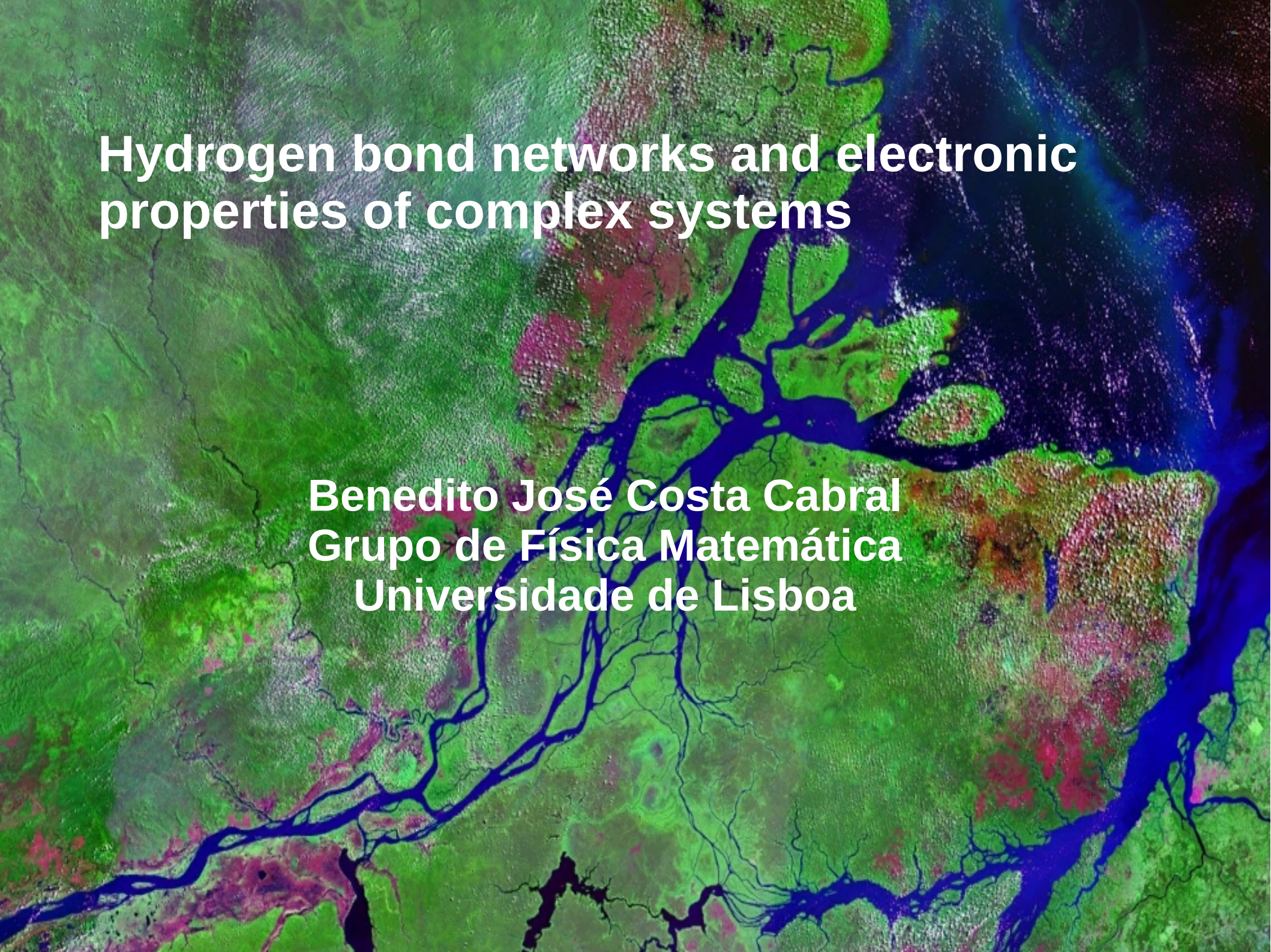

Hydrogen bond networks and electronic properties of complex systems

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Universidade de Lisboa

Parabéns Dino pelos seus extraordinários 70 anos

Outline

- **Hydrogen bond, hydrogen bond networks, and electronic properties**
- **Statistical Mechanics Sampling (BOMD)**
- **Applications**
- **Small water clusters; liquid hydrogen cyanide (HCN)**
- **Conclusions**
- **Acknowledgments**

Hydrogen bond, hydrogen bond networks, and electronic properties

Nature of the HB: complex interaction determined by charge interactions, dispersion interactions, many-body polarization effects, and charge transfer.

Hydrogen bond properties

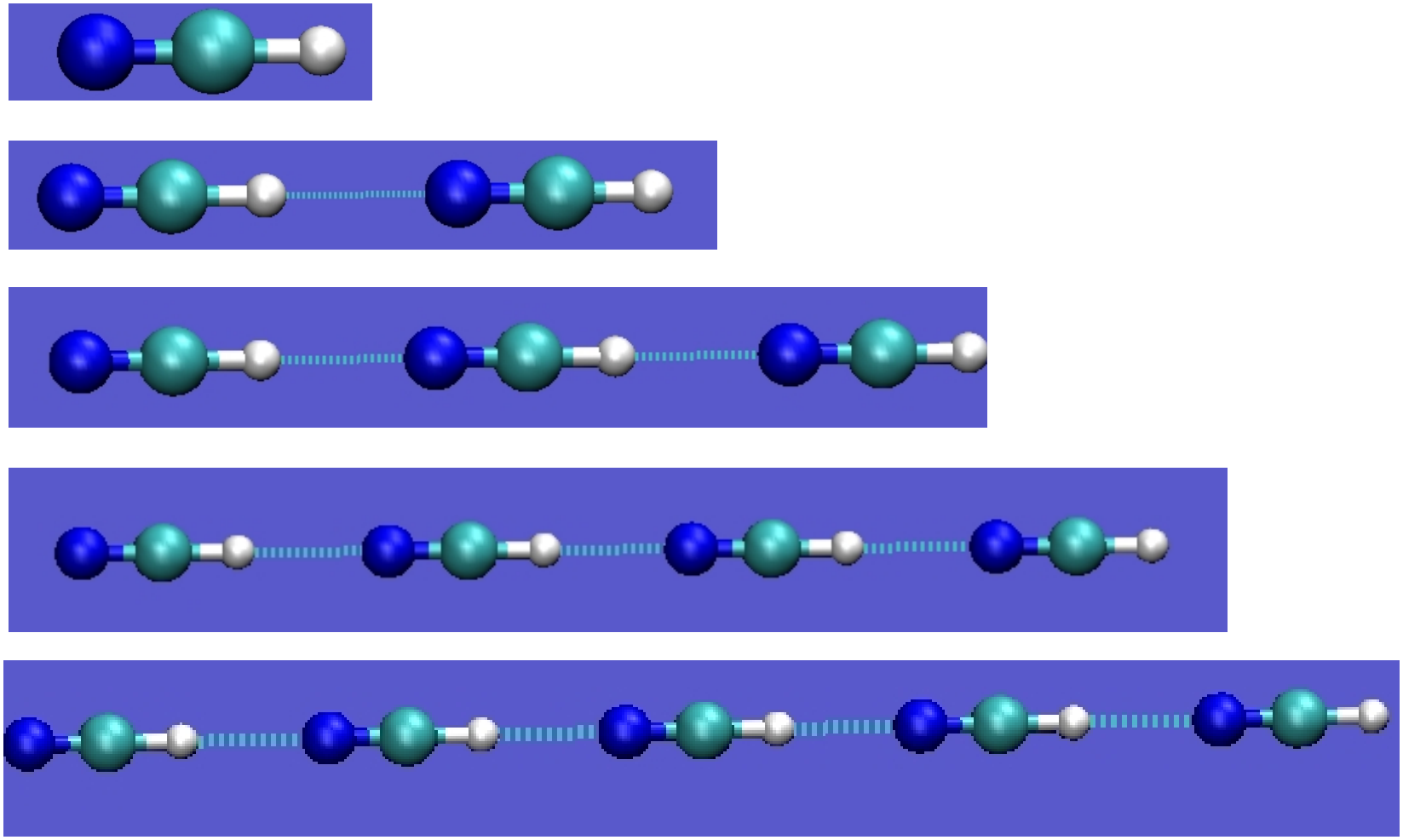
Directionality, anisotropy or strong orientational order

Cooperativity: many-body polarization effects

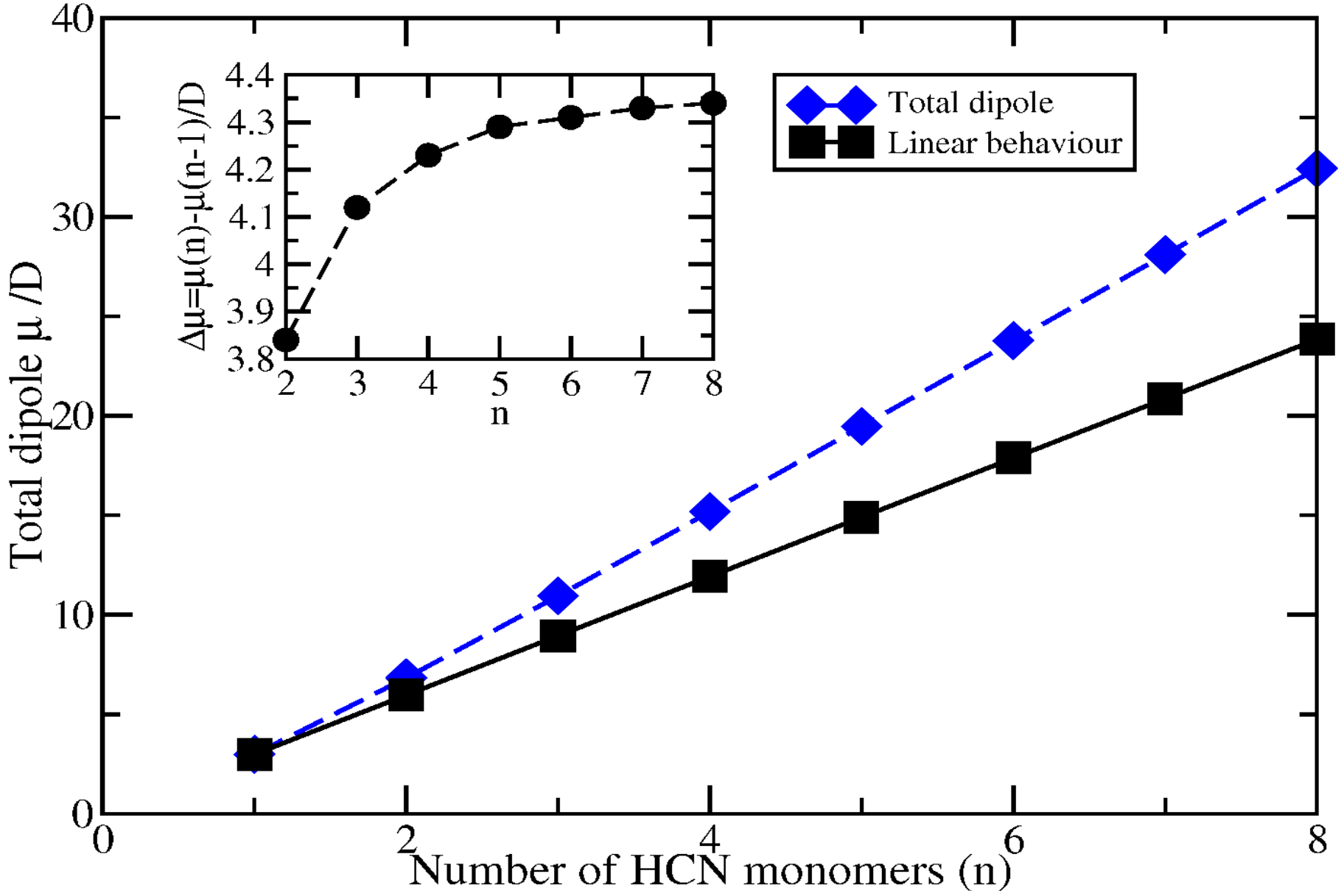
Electronic density reorganization: charge transfer

Directionality, anisotropy or strong orientational order

HCN linear chains



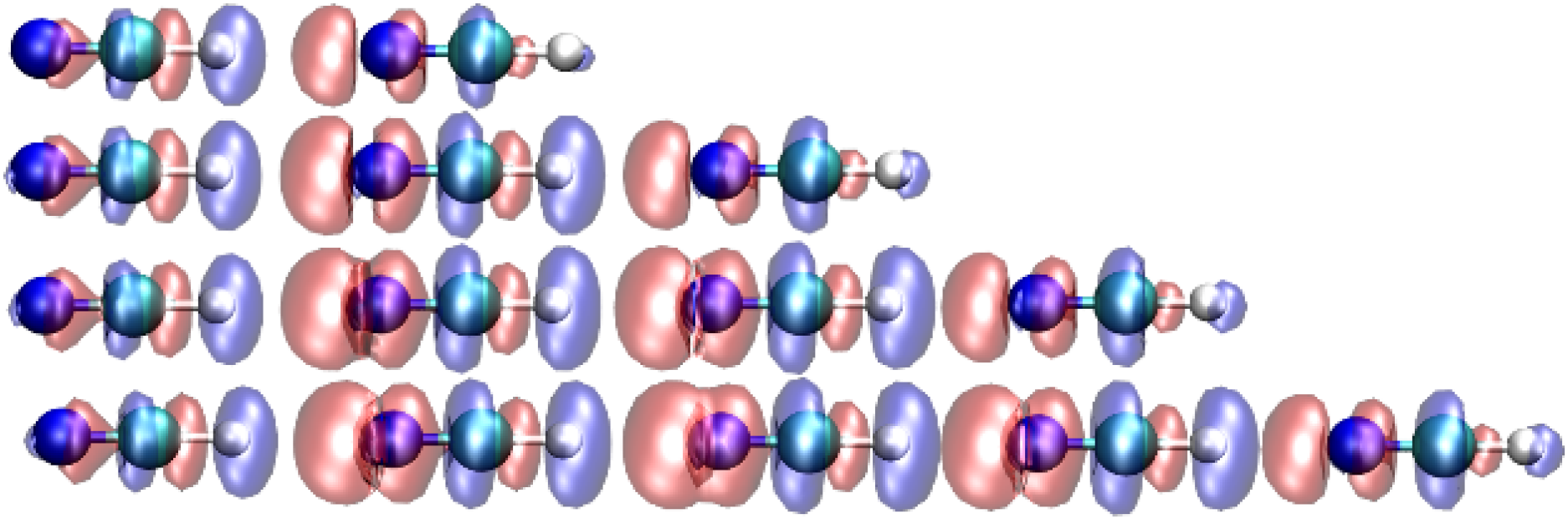
Cooperativity: many-body polarization effects



Electronic density reorganization: charge transfer

HCN linear chains: electronic density differences

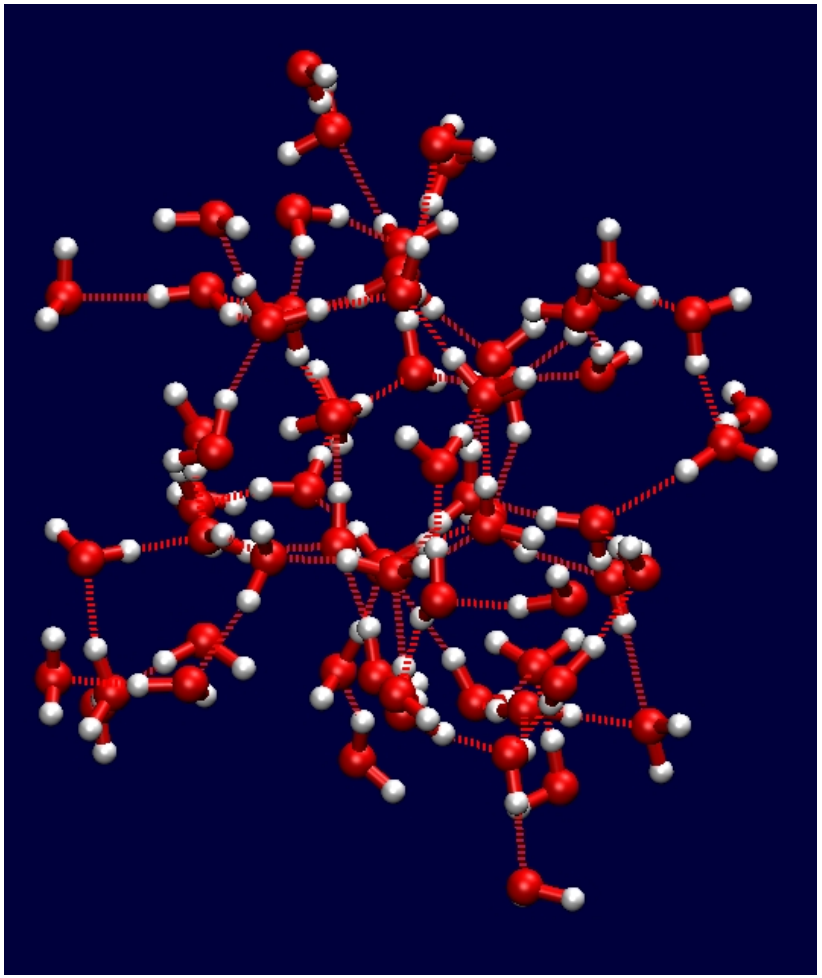
$$\Delta\rho_{\mathrm{n}}(\mathrm{r}) = \rho_{\mathrm{n}}^{\mathrm{T}}(\mathrm{r}) - \sum_{\mathrm{k}=1}^{\mathrm{n}} \rho_{\mathrm{k}}(\mathrm{r})$$



Hydrogen bond and HB networks

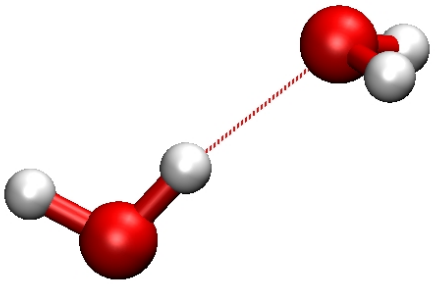
The most important liquid for life (water) is characterized by the presence of a hydrogen bond network

Electronic density fluctuations of the HB network determine the dynamics of (bio)chemical processes in water



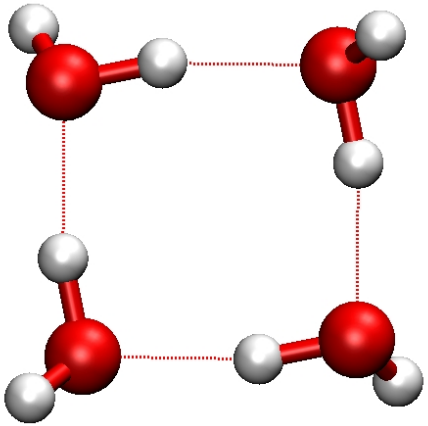
Hydrogen bonding (in small water clusters): geometric criterion

d[O-O] < 3.5 Angstroms; angle[OOH] < 25 Degrees



a

d



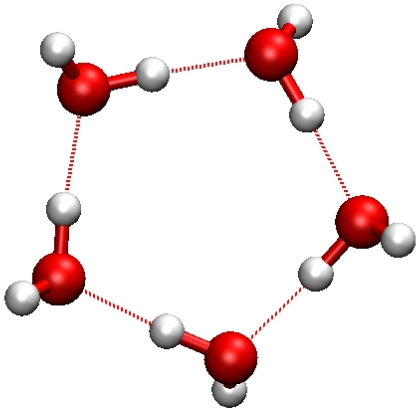
ad

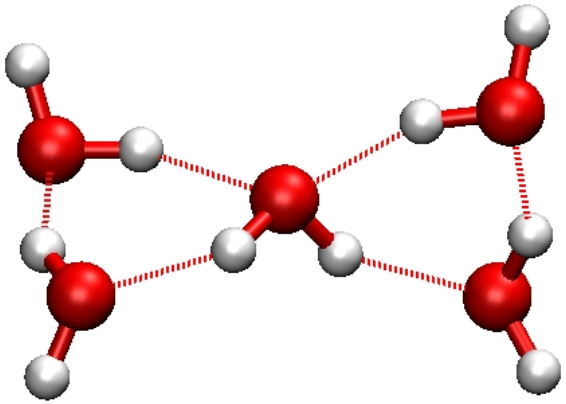
ad

ad

ad

5 x ad

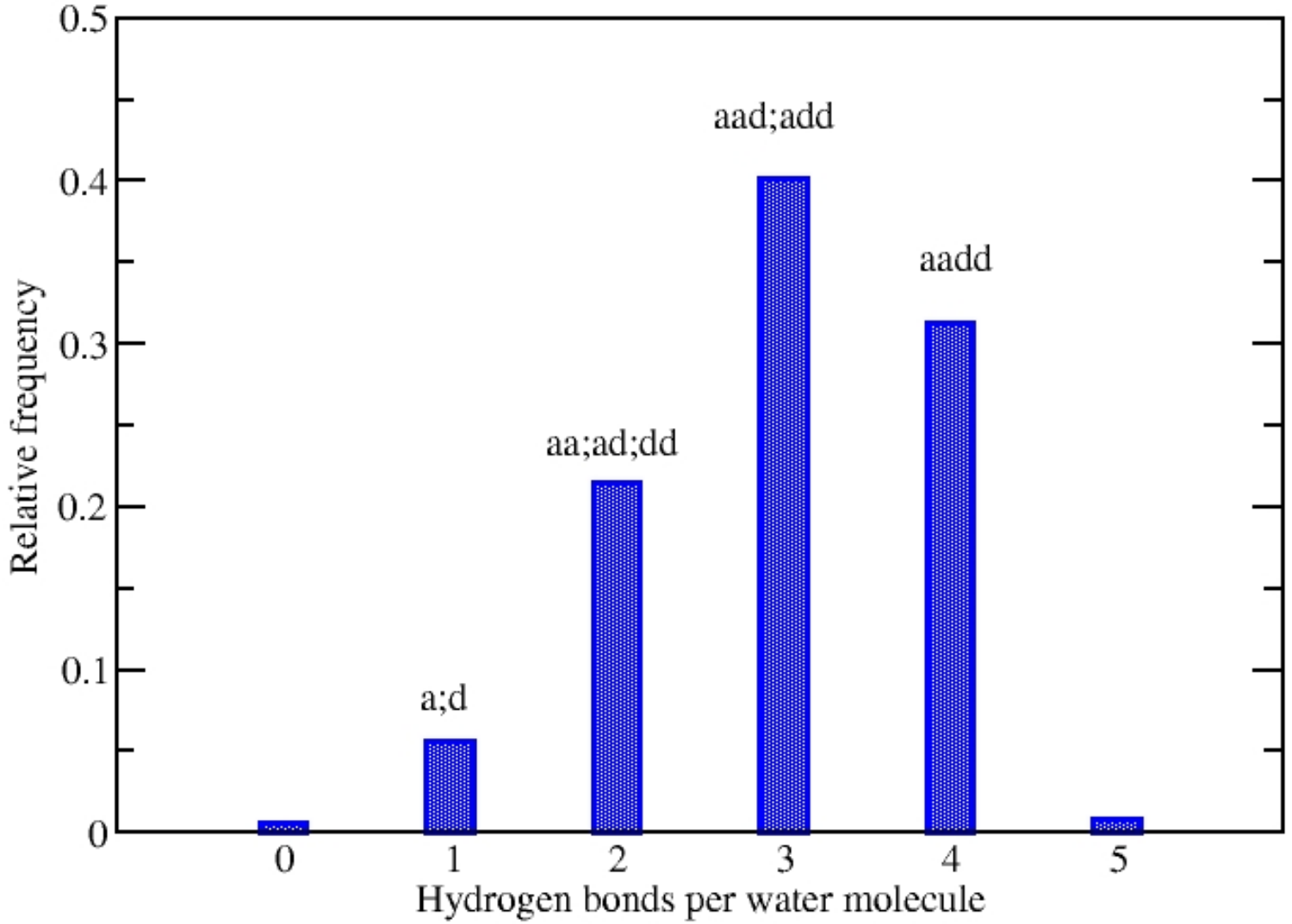




4 x ad

aadd

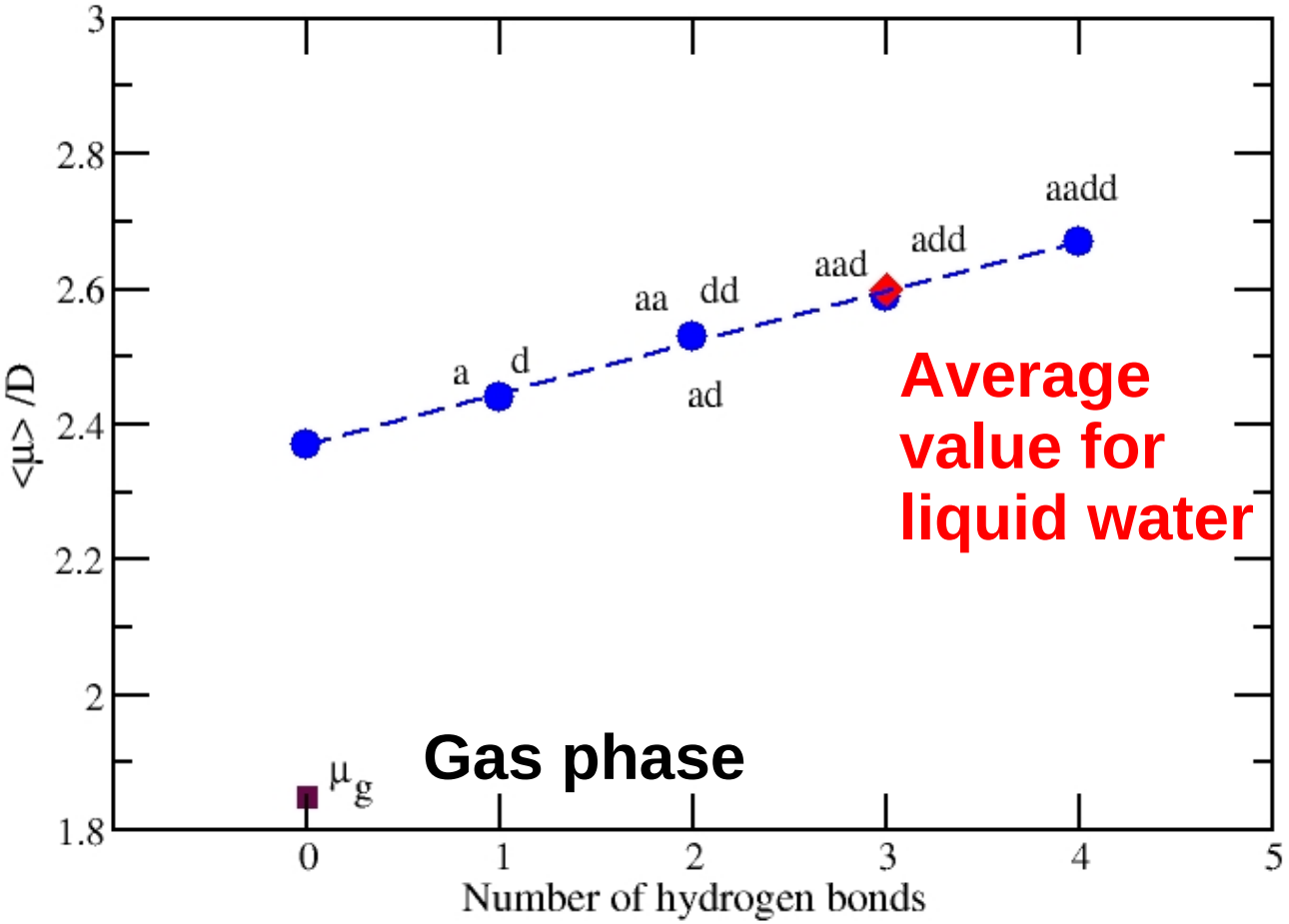
Distribution of hydrogen bonds in liquid water at ambient conditions



3 (aad;add) and 4 (aadd) HBs are dominant at ambient conditions

Relationship between the local organization of the network and electronic properties of water

Average monomeric dipole moment in liquid water

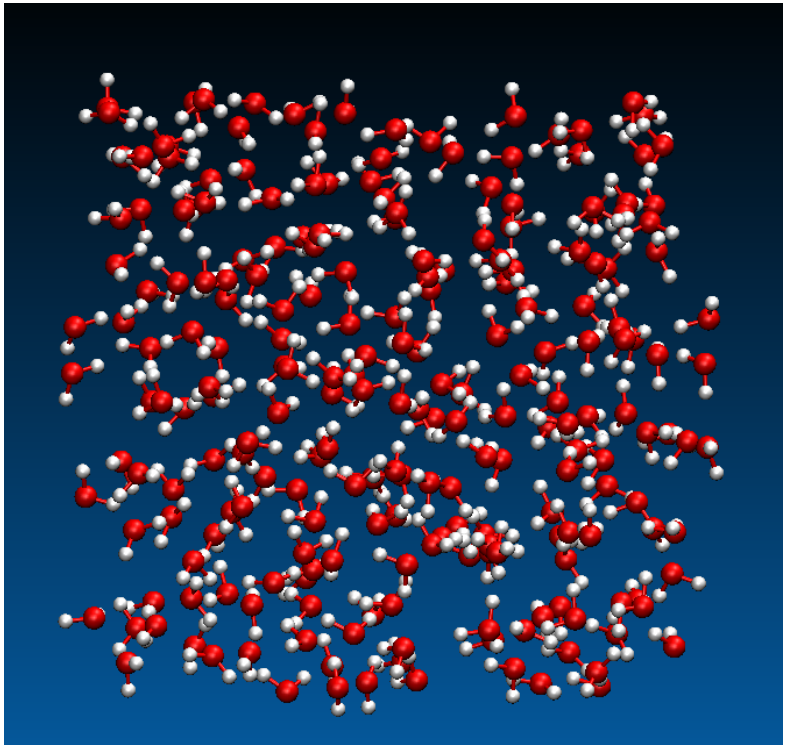


Electronic polarization increases linearly with the number of hydrogen bonds

Statistical mechanics sampling

Born-Oppenheimer molecular dynamics

$$\{\mathbf{R_A}\} \equiv (\mathrm{R_1}, \mathrm{R_2}, \cdots, \mathrm{R_M})$$



$$\hat{\mathrm{H}} = \sum_{\mathrm{a}=1}^{\mathrm{M}} \frac{\mathrm{P_a^2}}{2\mathrm{m_a}} + \sum_{\mathrm{i}=1}^{\mathrm{N}} \frac{\hat{\mathrm{p}}_\mathrm{i}}{2\mathrm{m_i}} + \mathrm{V}(\{\mathbf{r_i}\}; \{\mathbf{R_A}\})$$

$$\mathrm{U}(\mathrm{R_1}, \mathrm{R_2}, \cdots, \mathrm{R_M}) = < \Psi(\{\mathbf{r_i}\}; \{\mathbf{R_A}\}) | \hat{\mathrm{H}} | \Psi(\{\mathbf{r_i}\}; \{\mathbf{R_A}\}) >$$

$$\mathbf{F_a} = -\nabla_{\mathbf{R_a}} \mathrm{U}(\{\mathbf{R_a}\})$$

Applications

Hydrogen bond network of a (small) water cluster [$(H_2O)_{32}$]

- **Electronic properties of liquid hydrogen cyanide (HCN)**

Hydrogen bond network of a (small) water cluster

Changes of the HB network from the interior (bulk water) to the cluster surface (gas)

Identification of a moiety of "acceptor-only" water molecules (X-ray experiments) at the water surface.

K.R. Wilson et al *JPC B (*2001)

Vibrational spectrum of surface water predicts the presence of more than 20% of surface water molecules with a single H atom dangling away from the surface

Q. Du et al *PRL (1993*)

***Ab initio* MD of the liquid vapor-interface also predicted the existence of a surface "acceptor-only" moiety.**

I.-F. Kuo, C.J. Mundy *Science* (2004)

Hydrogen bond network of a (small) water cluster

All-electron Born-Oppenheimer Molecular Dynamics

NVE molecular dynamics

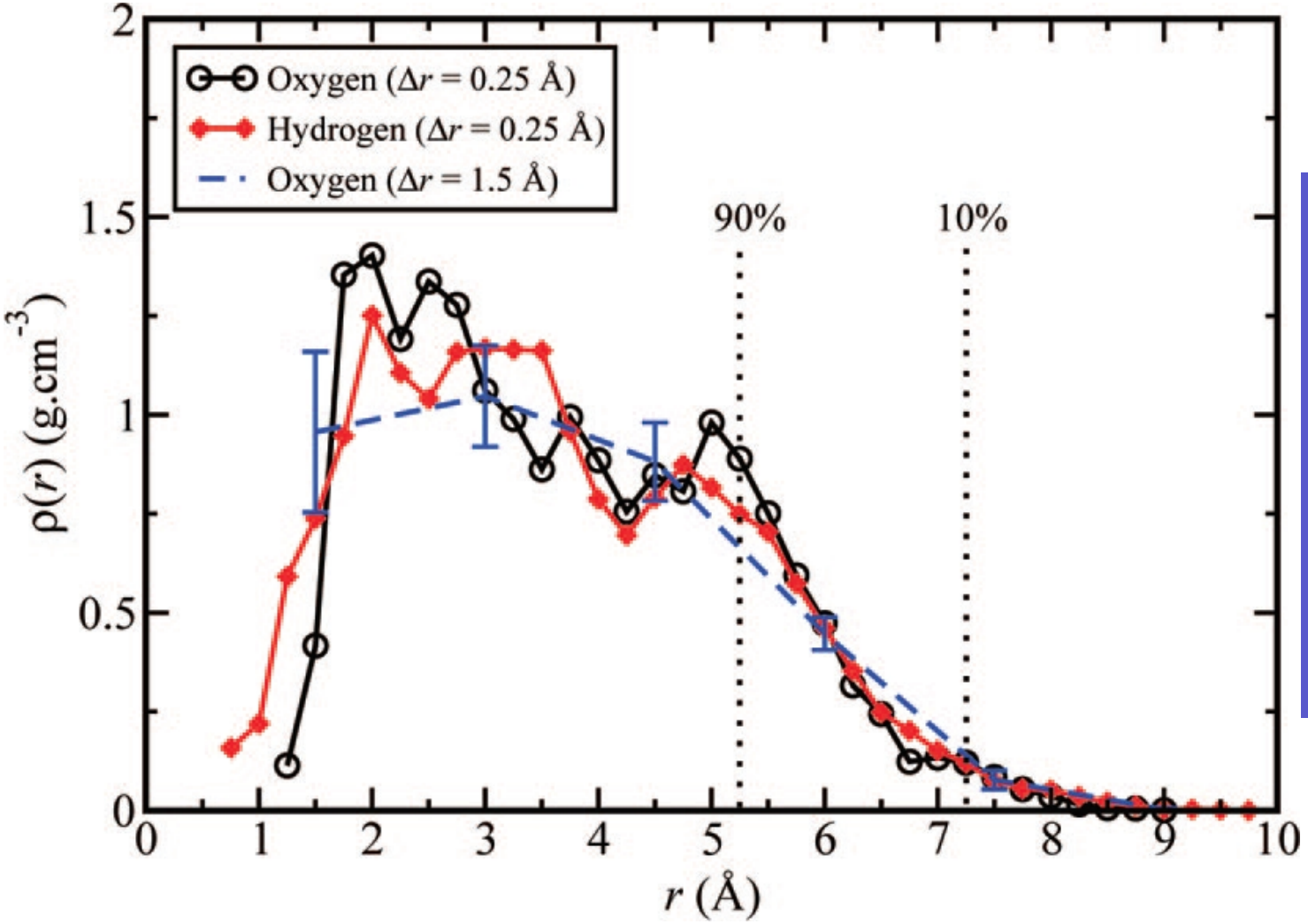
DFT energies and forces: Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional

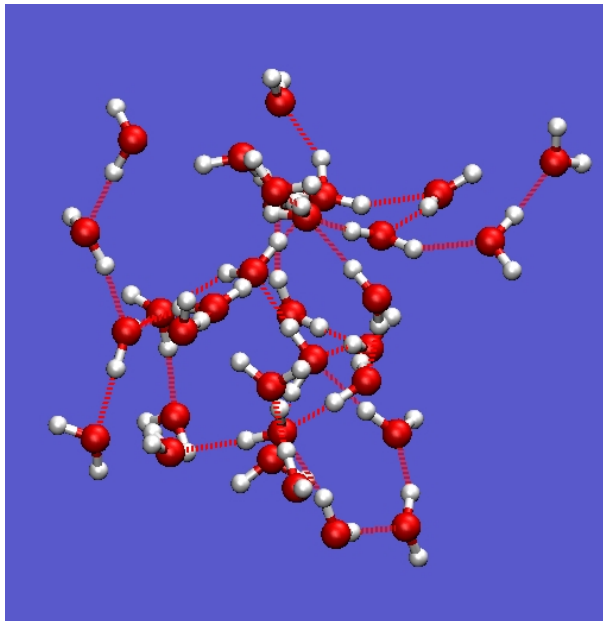
5 ps for equilibration followed by 16.5 ps for production; <T>=317 ± 24 K

N. Galamba and B.J.C. Cabral *JACS (*2008)

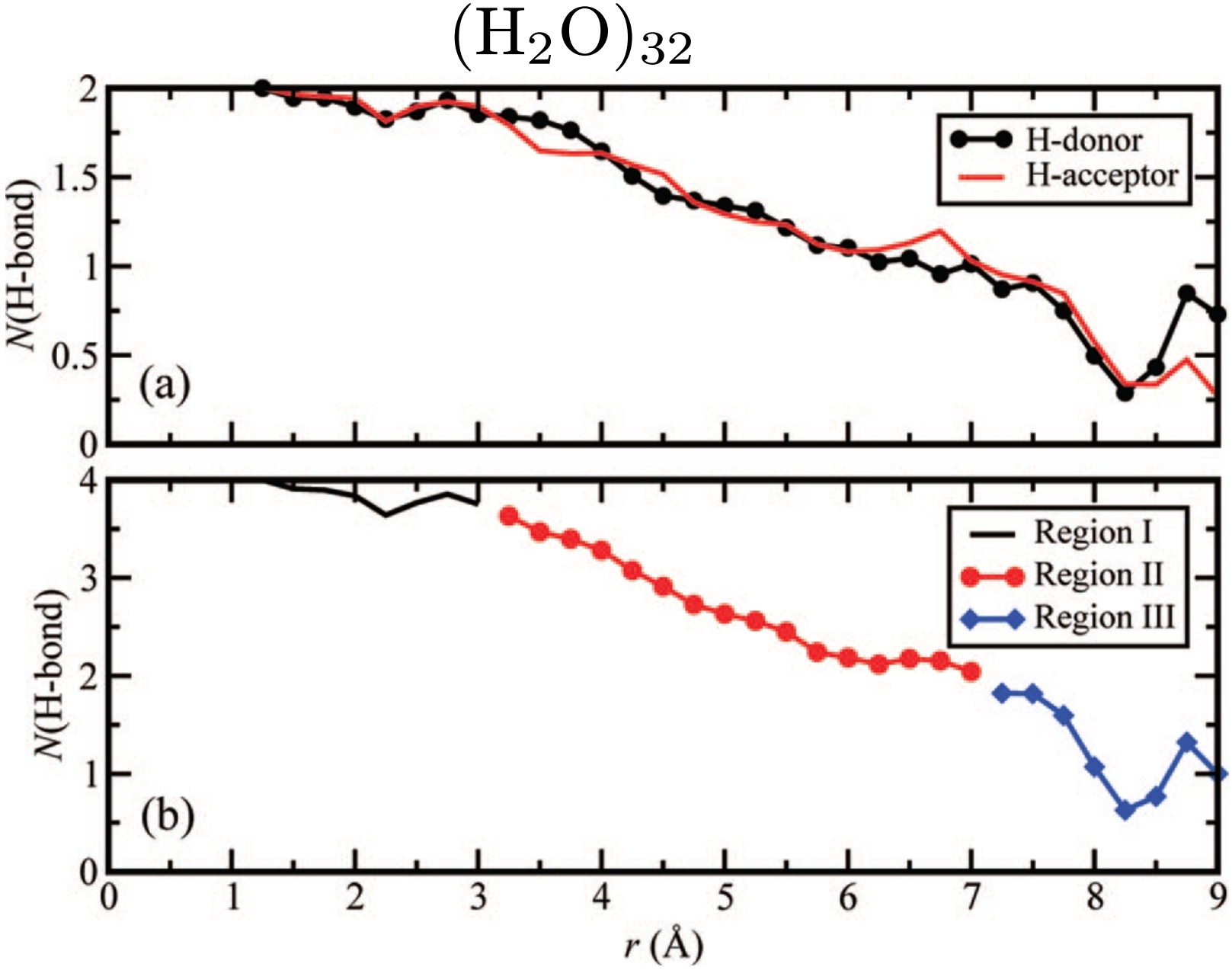
Hydrogen bond network of a (small) water cluster

$(H_2O)_{32}$

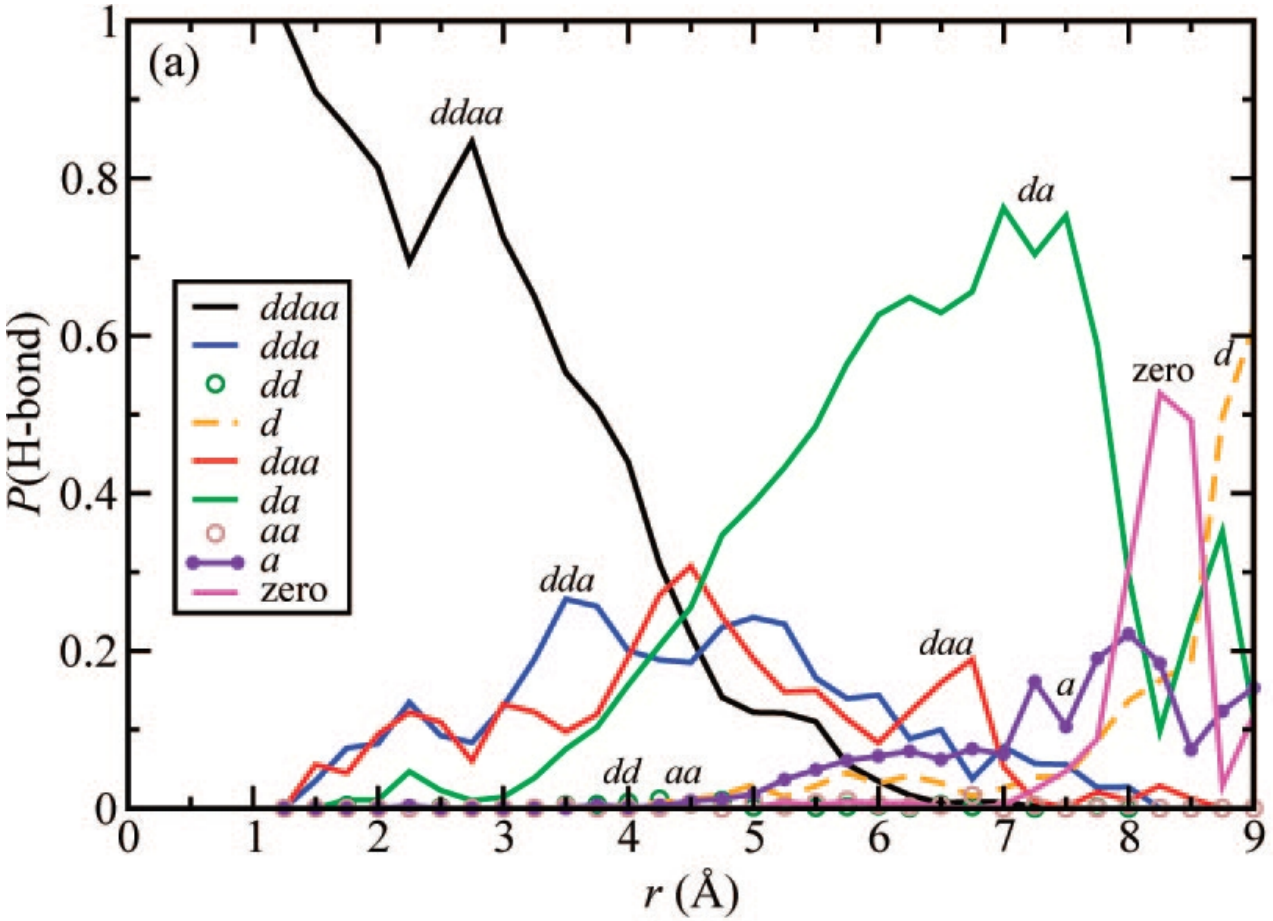




Hydrogen bond network of a (small) water cluster



Hydrogen bond network of a (small) water cluster

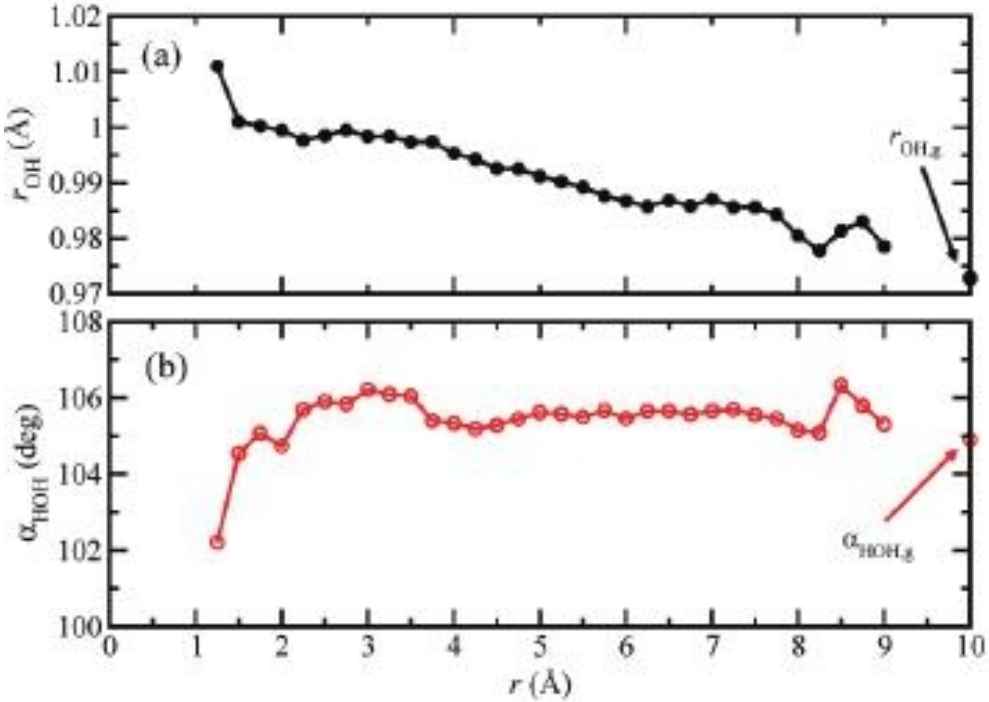


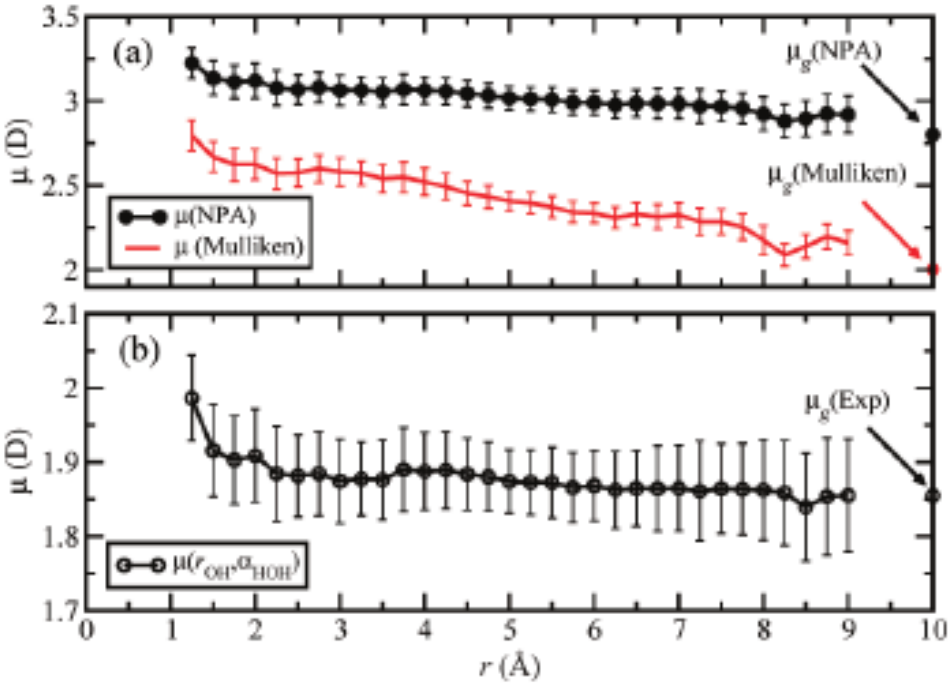
dd and aa arrangements are not abundant in any region of the cluster

da arrangements are largely dominant at the interface

Hydrogen bond network of a (small) water cluster

Polarization effects: the average monomeric water dipole moment in the cluster





The average monomeric dipole moment appears to be not very dependent on geometry deformations of water molecules in the HB network

Electronic properties of liquid HCN

Prebiotic and extraterrestrial species closely related to the origin of life.

C. N. Matthews, *Origins of life and Evol. Biosphere* (1991)

Strongly dipolar species that may form a complex HB bond network characterized by the presence of polymerized chains, ramified and cyclic aggregates.

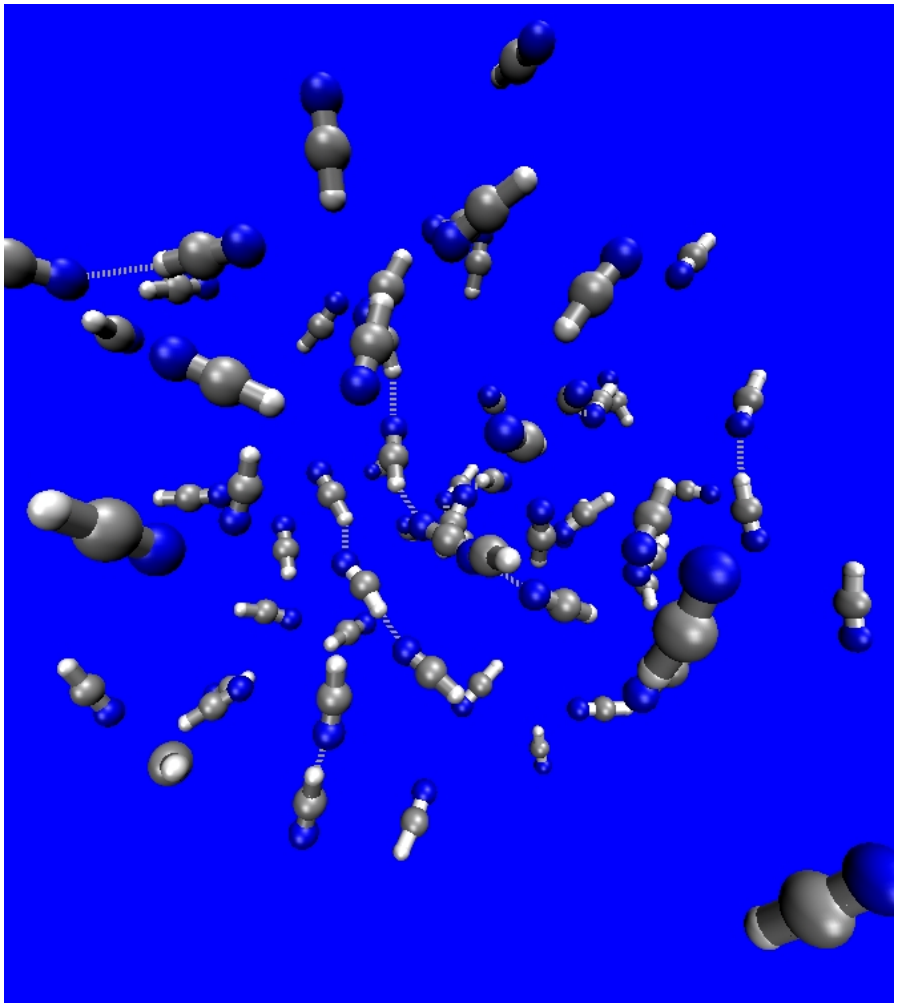
I. Mamajanov, J. Herzfeld, *J. Chem. Phys.* (2009)

Polar domains in strongly dipolar fluids

B.J.C. Cabral, *J. Chem. Phys.* (2000); D.P. Shelton, *J. Chem. Phys (2005)*

Electronic properties of liquid HCN

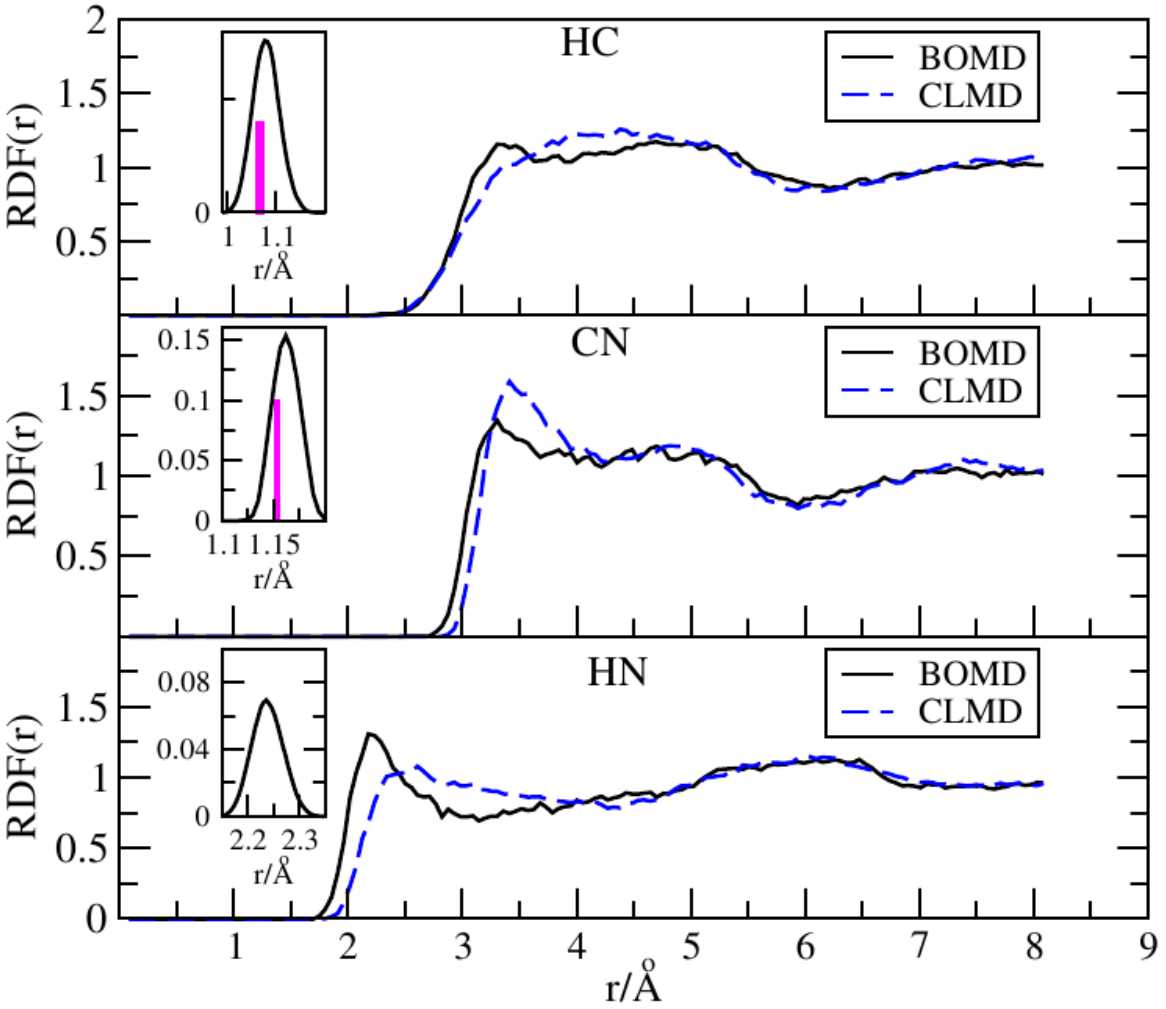
BOMD: timestep of 0.5 fs. (*NVT*) canonical ensemble at a density of 0.687 g.cm^{-3} and a target temperature of *T*=280 K (m.p *T*=260 K).



DFT/BOMD calculations were performed with a the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional

Electronic properties of liquid HCN

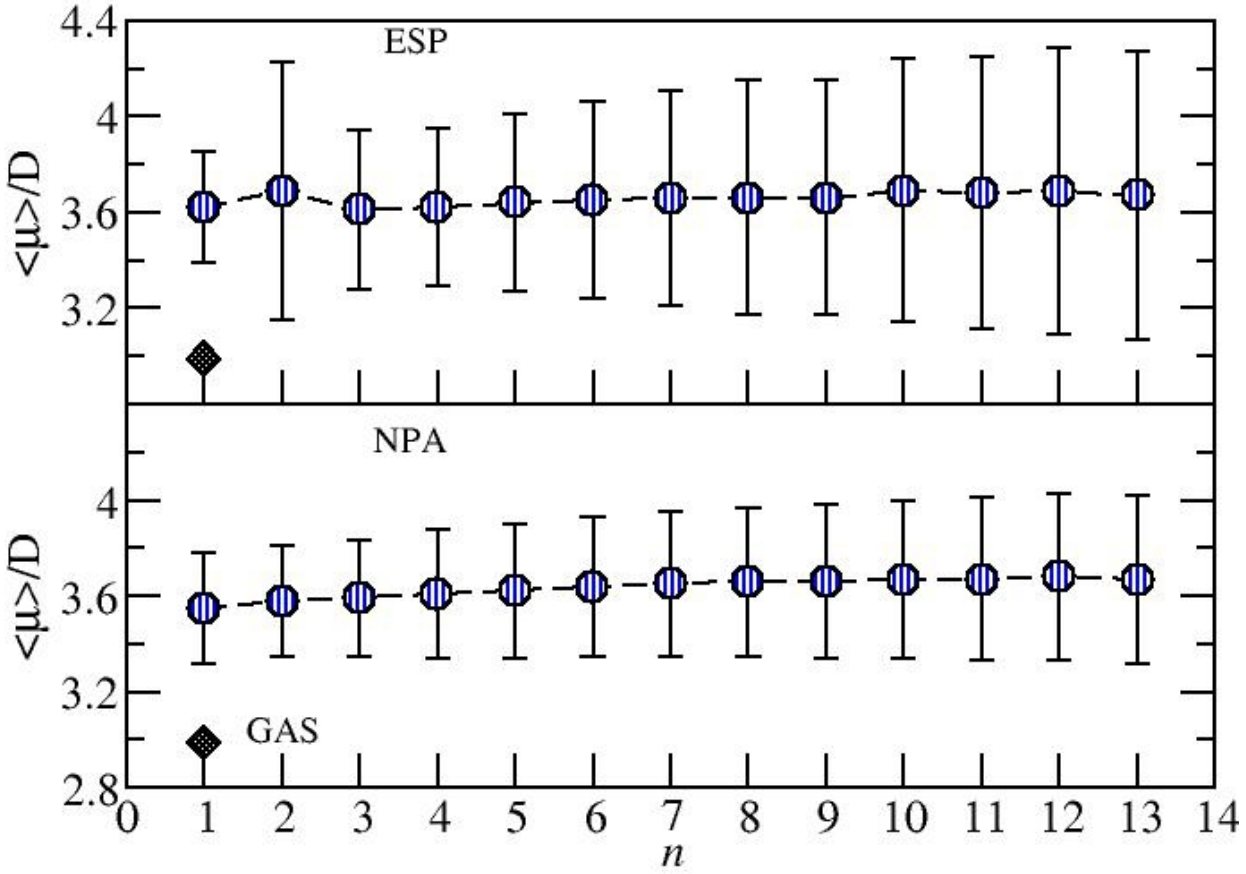
Structure of liquid HCN



The structure of liquid HCN is mainly characterized by the presence of linear dipole chains

Electronic properties of liquid HCN

Electronic polarization in liquid HCN: comparison with the gas phase



Significant change on the average monomeric dipole moment of HCN from 2.9 (G) to 3.6 D (L).

Electronic properties of liquid HCN

Electronic Absorption spectrum

Many body energy (MBE) decomposition schemes with electrostatic embedding

E.E. Dahlke, D.G. Truhlar *JCTC* (2007)
M. Chiba, D.G. Fedorov, K. Kitaura *JCP* (2007)
R.A. Mata, H. Stoll *CPL* (2008)

One-body approximation (with “excitonic coupling”) to the calculation of the first absorption band of water clusters

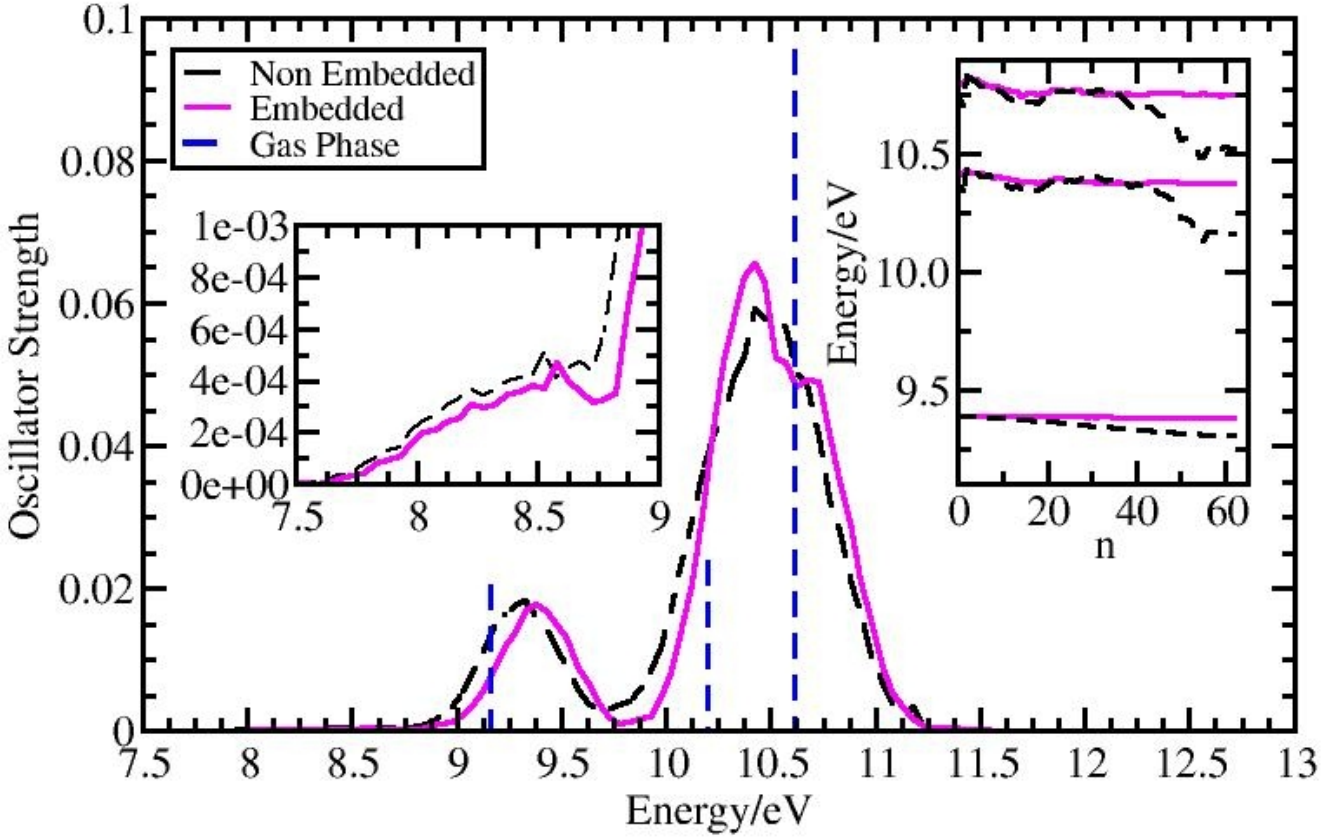
R.A. Mata, H. Stoll, B.J.C. Cabral *JCTC* (2009)

Extension to calculation of the full absorption spectra: application to liquid HCN

H. Martiniano, B.J.C. Cabral *CPL (*2013)

Electronic properties of liquid HCN

Electronic absorption in liquid HCN



The peak position of the first absorption band (L) is blue-shifted by 0.2 eV relative to the gas-phase value.

H. Martiniano, B.J.C. Cabral *CPL* (2013)

Conclusions/Perspectives

Sequential analysis of the electronic structure of configurations sampled by Born-Oppenheimer molecular dynamics can provide fundamental information on the relationship between the structure of hydrogen bond networks and electronic properties.

Coupling of many-body energy decomposition schemes to configurations generated by first principles (or classical) molecular dynamics make possible high level *ab initio* calculations of the electronic properties in condensed phases

Analysis of the electronic properties (and dynamics) of HB networks in interaction with charged and hydrophobic species

M. Mateus, N. Galamba, B.J.C. Cabral, J. Chem. Phys. 2012

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