ROMA TRE
UNIVERSITÀ DEGLI STUDI

THE ROLE OF HYDRATION IN CARBOHYDRATES PROPERTIES

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Roma, 22 Settembre 2015

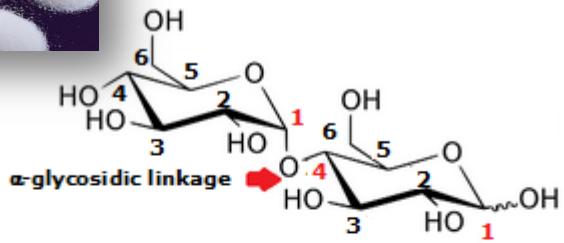
Outline

- **Scientific Issue**: atomic description of hydration can be useful to explain carbohydrates function (sweet taste response, bio-protection…)
- **Experimental results** from neutron diffraction with isotopic substitution combined with computer simulation
- **Conclusions**

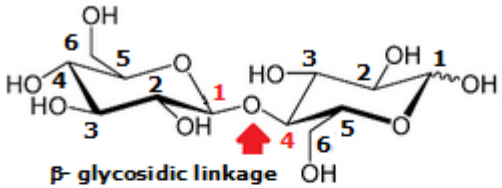
Structure-activity

- Why glucose is sweet?
- Why trehalose is an high efficiency bio-protectant agent?
- Why cellobiose is not sweet ?
- What is the role of atomic hydration to understand these properties?

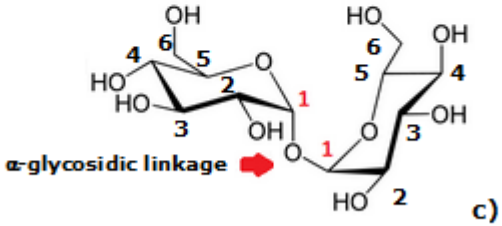
Carbohydrates



Maltose a)

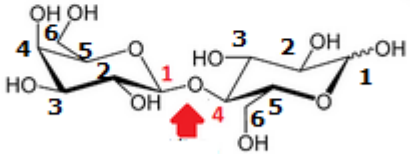


Cellobiose b)



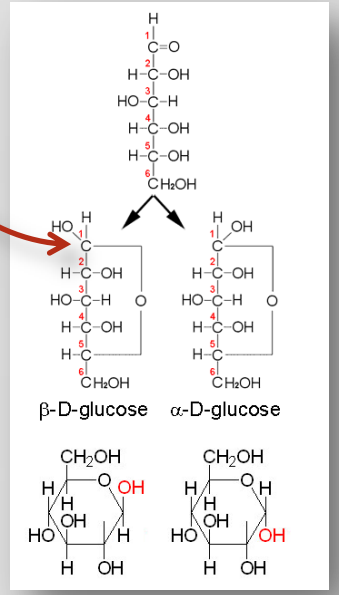
c)

Trehalose

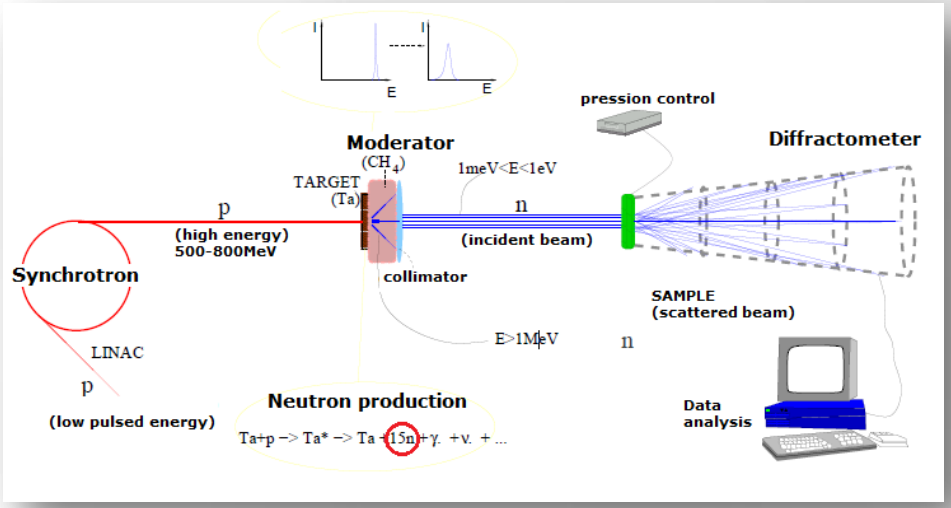


d)

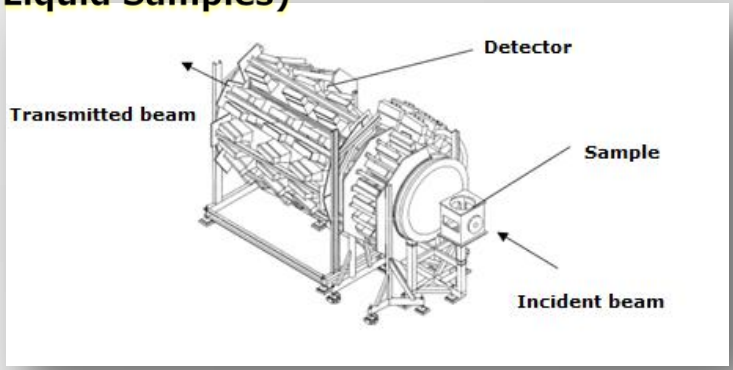
Lactose



Experimental setup for NDIS



SANDALS (Small Angle Neutron Diffractometer for Amorphous and Liquid Samples)



High energy neutrons:
$0.05Å \leq \lambda \leq 5.0Å$

Wide Q range:
$0.1Å^{-1} \leq Q \leq 50Å^{-1}$

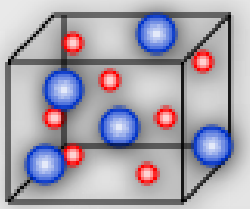
Science & Technology Facilities Council
ISIS

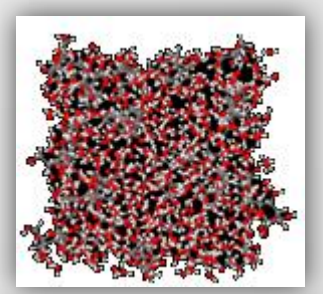
$$\left(\frac{d\sigma}{d\Omega}\right)_{tot} = \left(\frac{d\sigma}{d\Omega}\right)_{distinct} + \left(\frac{d\sigma}{d\Omega}\right)_{self}$$

$$= \sum_{\alpha} c_\alpha b_\alpha{}^2 \left(1 + P(Q,\vartheta) + F(Q)\right)$$

EPSR

The short range structure of the sample (water+solute) can be obtained by using **EPSR** which is a Monte Carlo algorithm, updating the interatomic potential according to the data.





1. Simulation box: ρ, c_α

2. Reference potential

$$U^{ref}{}_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right] + \frac{q_\alpha q_\beta}{4\pi\varepsilon r}$$

-----Lennard-Jones potential---- *---Coulomb potential---*

3. Initial atomic configurations

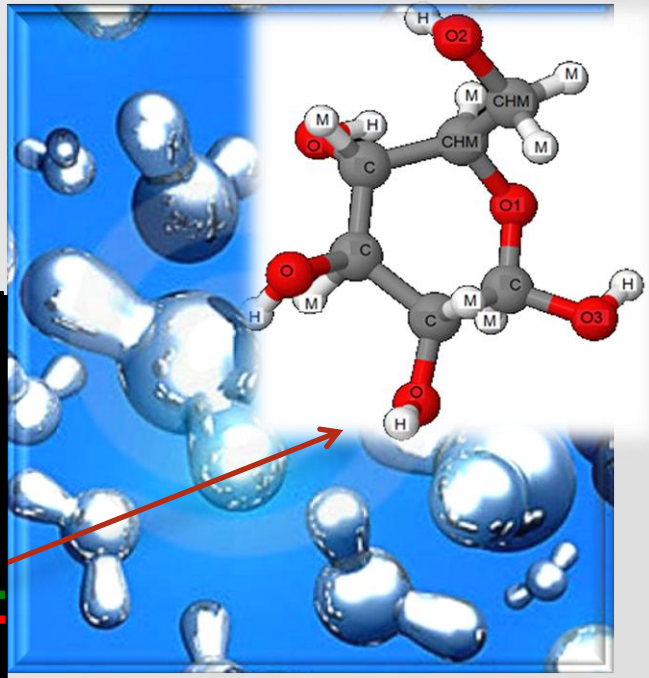
- Movements minimizing energy
- New atomic configurations
- Comparison with experimental structure factors
- Updating pair potential

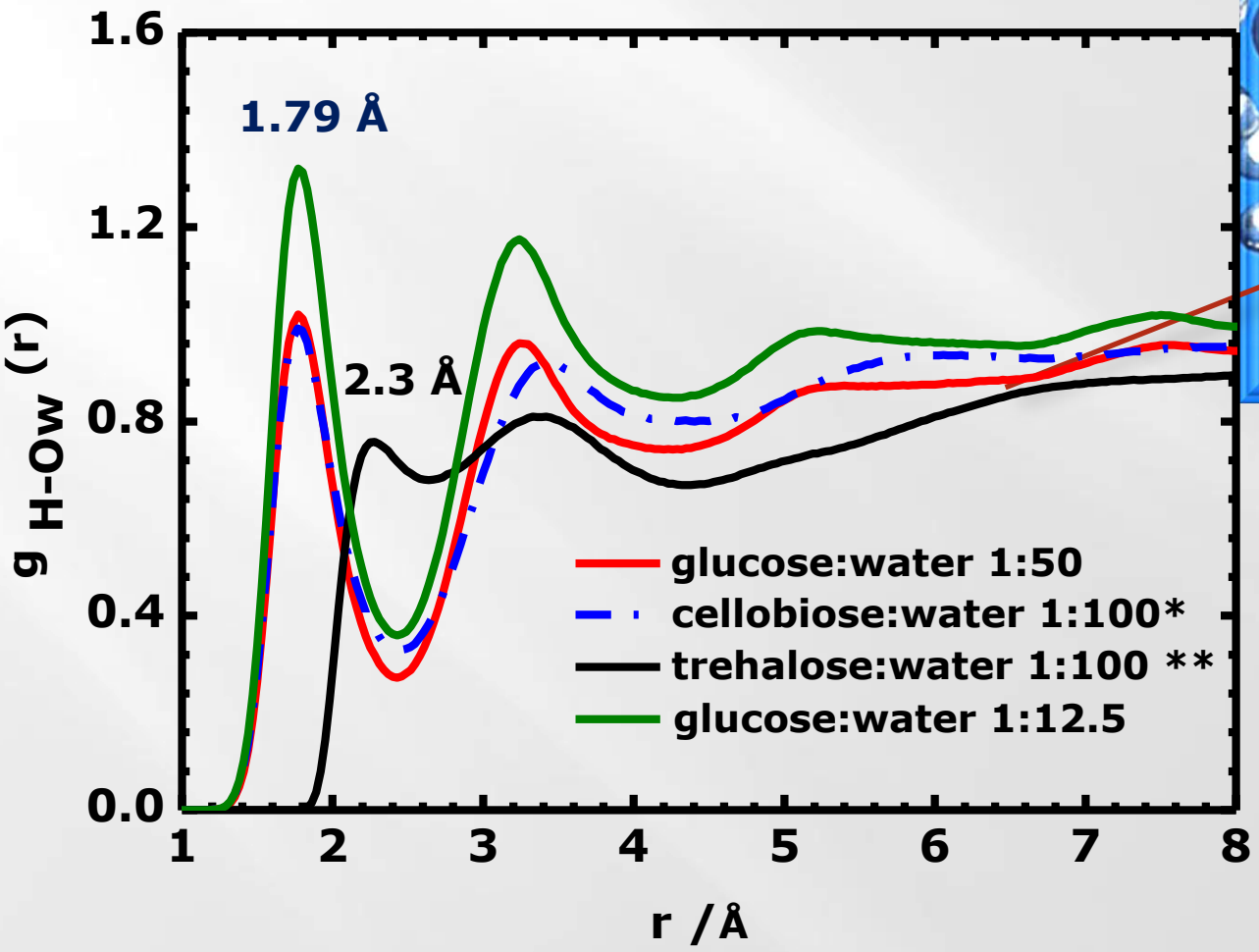
To obtain Radial Distribution Function RDF

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 \rho} \int_0^{\infty} Q^2 dQ (S_{\alpha\beta}(Q) - 1) \frac{\sin(Qr)}{Qr}$$

$$n^{\beta}{}_{\alpha}(r) = 4\rho\pi c_{\beta} \int_{r1}^{r2} r^2 g_{\alpha\beta}(r) dr$$

Different Hydration of hydroxyl-group

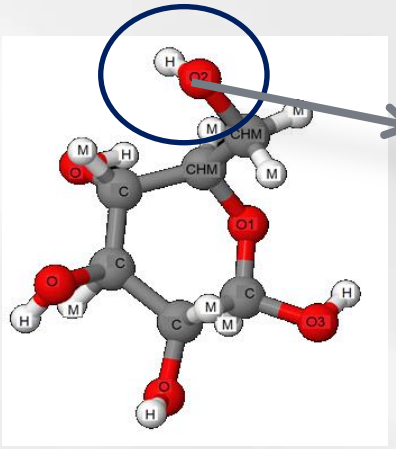


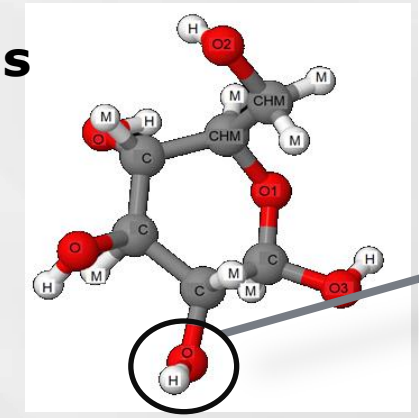


**W.B.O'Dell, D.C. Baker, S.E. McLain, PLoS ONE, 7, 10 (2012).*

***S.E.Pagnotta et al, J. Phys. Chem. B, 114, 4904–4908 (2010).*

Spatial density function (SDF)

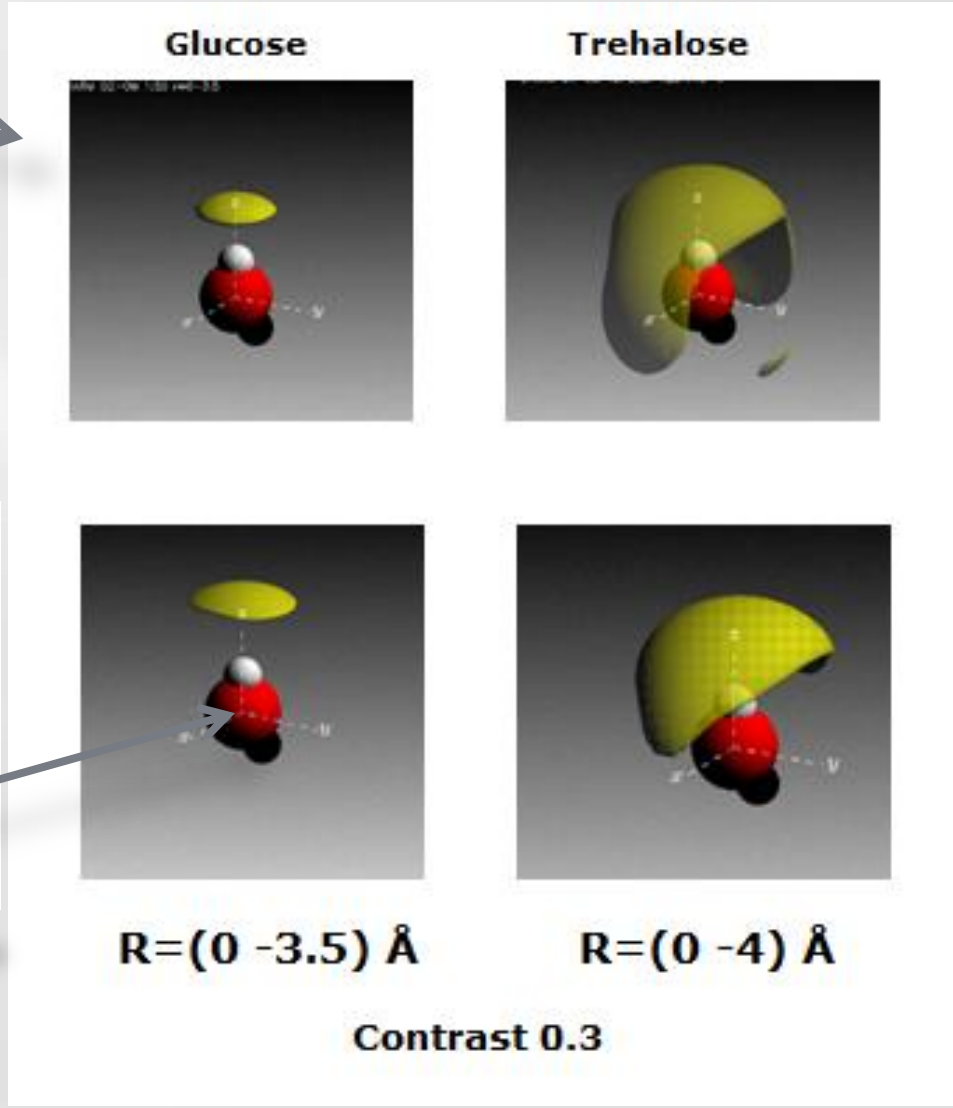




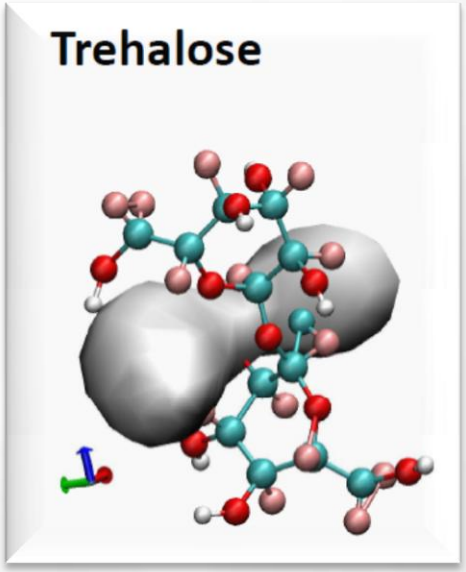
Different H -bonds with water:

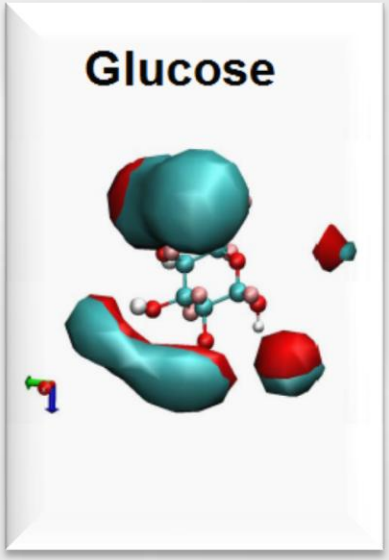
-<u>different directionality</u>

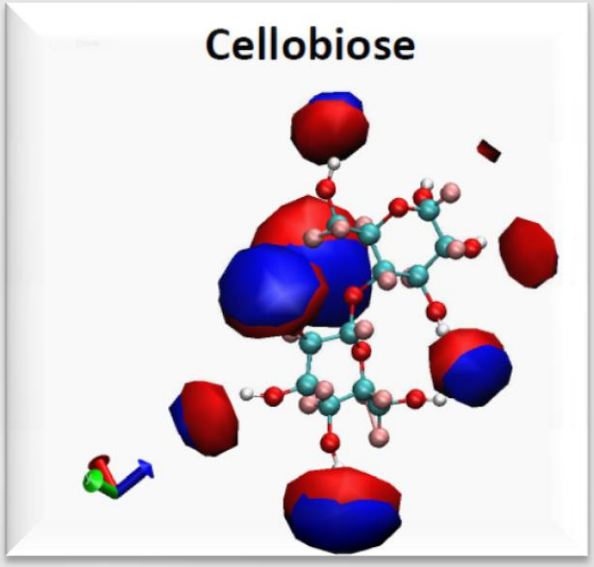
-<u>different distance</u>



Spatial density maps (SDM)





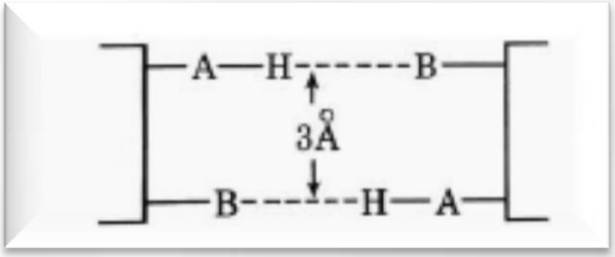


S.E.Pagnotta et al, J. Phys. Chem. B, 114, 4904–4908 (2010).

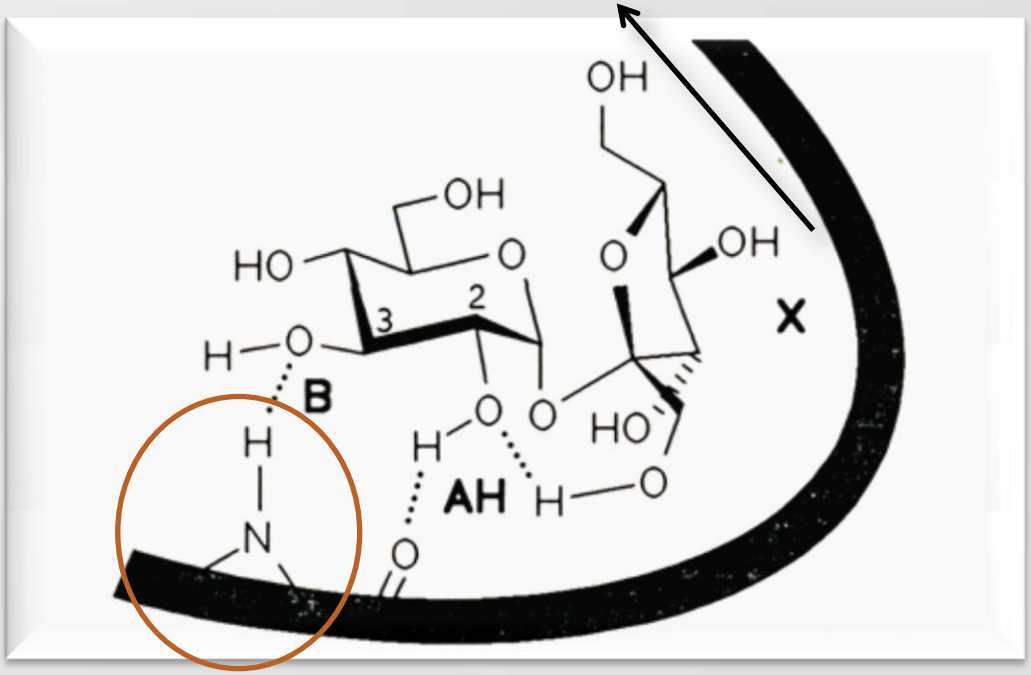
W.B.O'Dell, D.C. Baker, S.E. McLain, PLoS ONE, 7, 10 (2012).

"Triangle" of sweetness

$$2.51\ \text{Å} < A - B < 4\ \text{Å}$$



Shallenberger, 1963

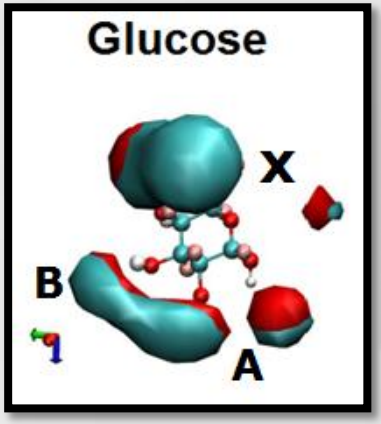


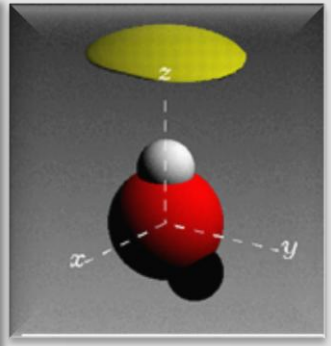
- **Inter- and intra-molecular H bonds;**
- **hydrophilic and hydrophobic sites;**
- **flexibility;**
- **single glucose ring required.**

Different hydration-different function

Sweet because:

- has the right structure for the taste bud receptor;
- makes directional H-bonds;
- fits the AH-B-X model.



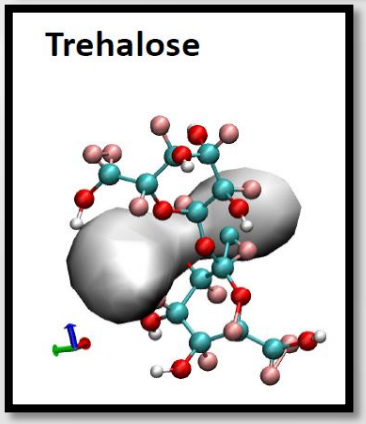


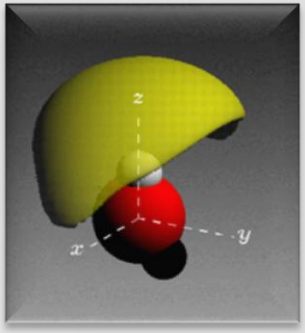
Not sweet because:

- doesn't make directional H-bonds;
- doesn't fit the AH-B-X model.

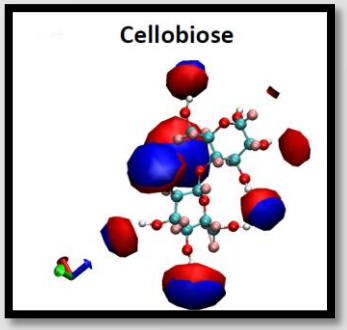
But

Could explain trehalose-trehalose interaction (Bio-protection??)





Not sweet because has no flexibility (fiber component)



Conclusion

- **Different atomic hydration can be the key to explain functionality of some sugars.**

- **Water mediated H-bonds are useful to predict sweet response.**

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Prof. Fabio Bruni

Prof. Maria Antonietta Ricci

Sylvia McLain

Luis Carlos Pardo

THANKS FOR YOUR ATTENTION

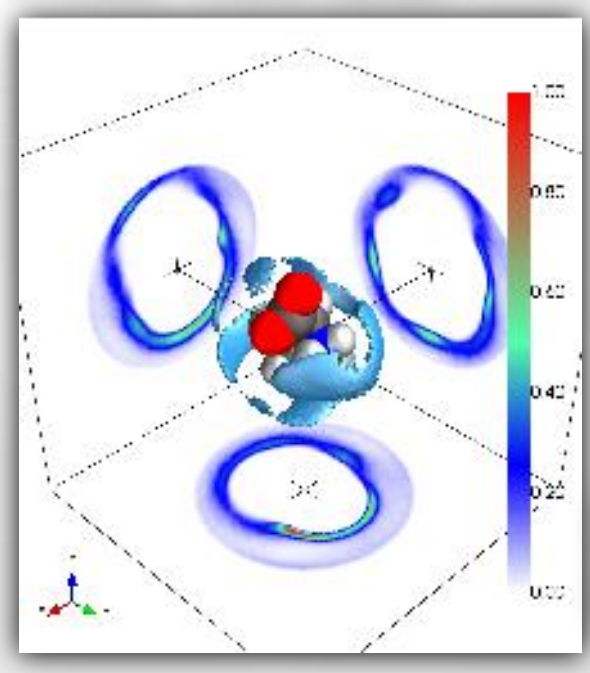
Angula

- Collects many EPSR or MD configurations to determine:

1. Position and orientation of neighboring solute and water molecules around a central reference molecule;

2. Spatial density maps (SDMs) that show the probability density of one molecule around another in three dimensions.

Proline–water SDMs

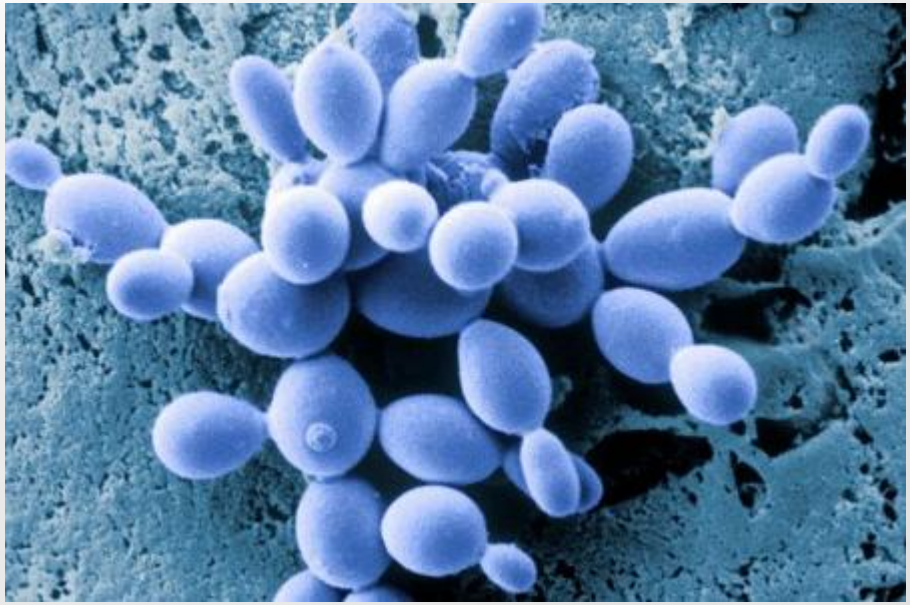


https://gcm.upc.edu/en/members/luis-carlos/angula/ANGULA

Bioprotection

Some sugars protect cell membranes from stress induced by dehydration or osmotic/termic shock. Trehalose is the best performer in this sense.

Saccharomyces cerevisiae



Multiatomic system and EPSR(Empirical potential structure Refinement)

$$\left(\frac{d\sigma}{d\Omega}\right)_{tot} = \left(\frac{d\sigma}{d\Omega}\right)_{distinct} + \left(\frac{d\sigma}{d\Omega}\right)_{self}$$

$$= \sum_{\alpha} c_\alpha b_\alpha{}^2 \left(1 + P(Q,\vartheta) + F(Q)\right)$$

Static structure factor

Total structure factor

$$F(Q) = \sum_{\alpha,\beta\geq\alpha} \left(2 - \delta_{\alpha\beta}\right) c_\alpha c_\beta \overline{b_\alpha b_\beta} \left(S_{\alpha\beta}(Q) - 1\right)$$

Partial structure factor

Scattering length for differnt atoms (α, β)

Atomic fraction

Caso H/D

$$F_{H_2O}(Q) = c_H{}^2 \langle b_H \rangle^2 S_{HH}(Q) + c_X{}^2 \langle b_X \rangle^2 S_{XX}(Q) + 2 c_H c_X \langle b_H \rangle \langle b_X \rangle S_{XH}(Q)$$

$$F_{D_2O}(Q) = c_D{}^2 \langle b_D \rangle^2 S_{HH}(Q) + c_X{}^2 \langle b_X \rangle^2 S_{XX}(Q) + 2 c_D c_X \langle b_D \rangle \langle b_X \rangle S_{XH}(Q)$$

$$F_{HDO}(Q) = \langle b_{HD} \rangle^2 S_{HH}(Q) + c_X{}^2 \langle b_X \rangle^2 S_{XX}(Q) + 2 c_X \langle b_{HD} \rangle \langle b_X \rangle S_{XH}(Q)$$

con

$$\langle b_{HD} \rangle = c_H \langle b_H \rangle + (1 - c_H) \langle b_D \rangle = c_H \langle b_H \rangle + c_D \langle b_D \rangle$$