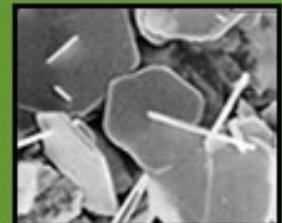


COMPUTATIONAL STUDY ON THE ONSET OF CALCIUM CARBONATE NUCLEATION

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**Mineral Nucleation & Growth Kinetics
Research Training Network**



Formation of CaCO₃ in aqueous solution

Mineralisation CaCO₃ as a potential route to CO₂ sequestration



The first step in the mineralisation of CaCO₃ is the **nucleation** of amorphous calcium carbonate (ACC) particles [1].

The details of the onset of nucleation are still unclear.

[1] (a) J. Bolze et al., *Langmuir* **18**, 8364 (2002). (b) D. Pontoni et al., *J. Phys. Chem. B* **107**, 5123 (2003) (c) Q. Shen et al, *J. Phys. Chem. B* **110**, 2994 (2006). (e) M. F. Michel et al., *Chem. Mater.* **20**, 4720 (2008).

Objectives

First principle calculations used to model the first stages of CaCO_3 nucleation from aqueous solution:

- Car Parrinello Molecular Dynamics
 - formation of CaCO_3 monomer in solution
 - hydration shell of CaCO_3 / CaHCO_3^+ .
- Static DFT and *ab-initio*
 - *tmd* stability of $[\text{Ca}(\text{HCO}_3)_m]^{2-m}$ in aqueous solution
 - mechanism of oligomerization

CPMD simulations

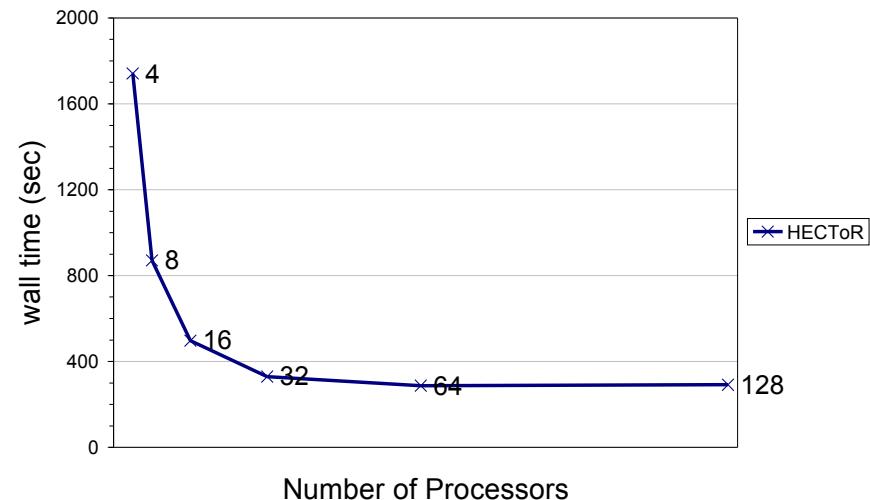
Quantum-ESPRESSO

P. Giannozzi et al., <http://www.quantum-espresso.org>

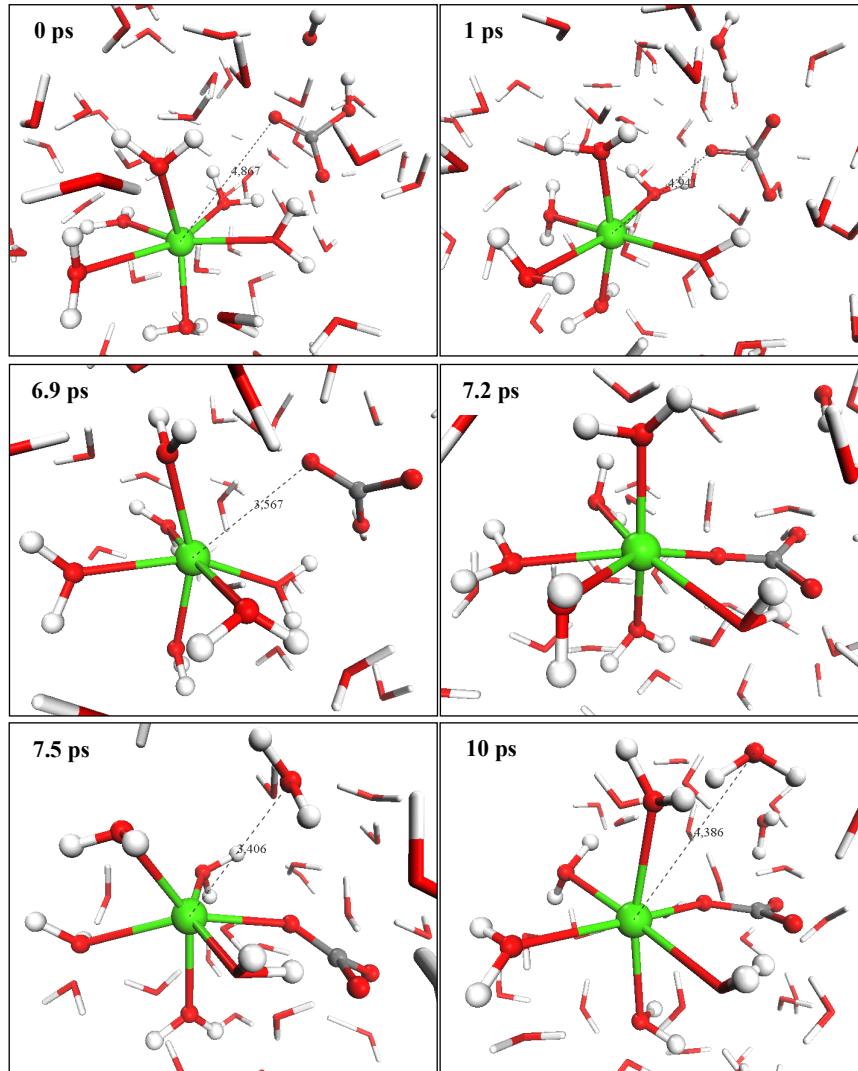
- PBE approximation for E_{xc}
- Ultrasoft PPs and PW basis set ($ecutwfc = 30.0$ Ryd)
- Fictitious electron mass $\mu = 600$ a.u. Time step $\delta t = 0.14$ fs
- NVT ensemble ($T = 400$ K)

Computational requirements of CPMD

- Simulation cell $[\text{Ca}^{2+} + 52 \text{ H}_2\text{O}]$ or $[\text{Ca(H)CO}_3 + 52 \text{ H}_2\text{O}]$
- 32-64 CPU (IBM Power5 processors 1.5 GHz clock rate / dual core AMD Opteron 2.8 GHz clock rate)
- 1 psec of CP molecular dynamics require $\sim 250 - 330$ CPU hours.
- Structural and dynamical analysis of a liquid system typically require a simulation period of ~ 20 psec
- Limited scalability of CPMD codes



Formation of the monomer of CaCO_3



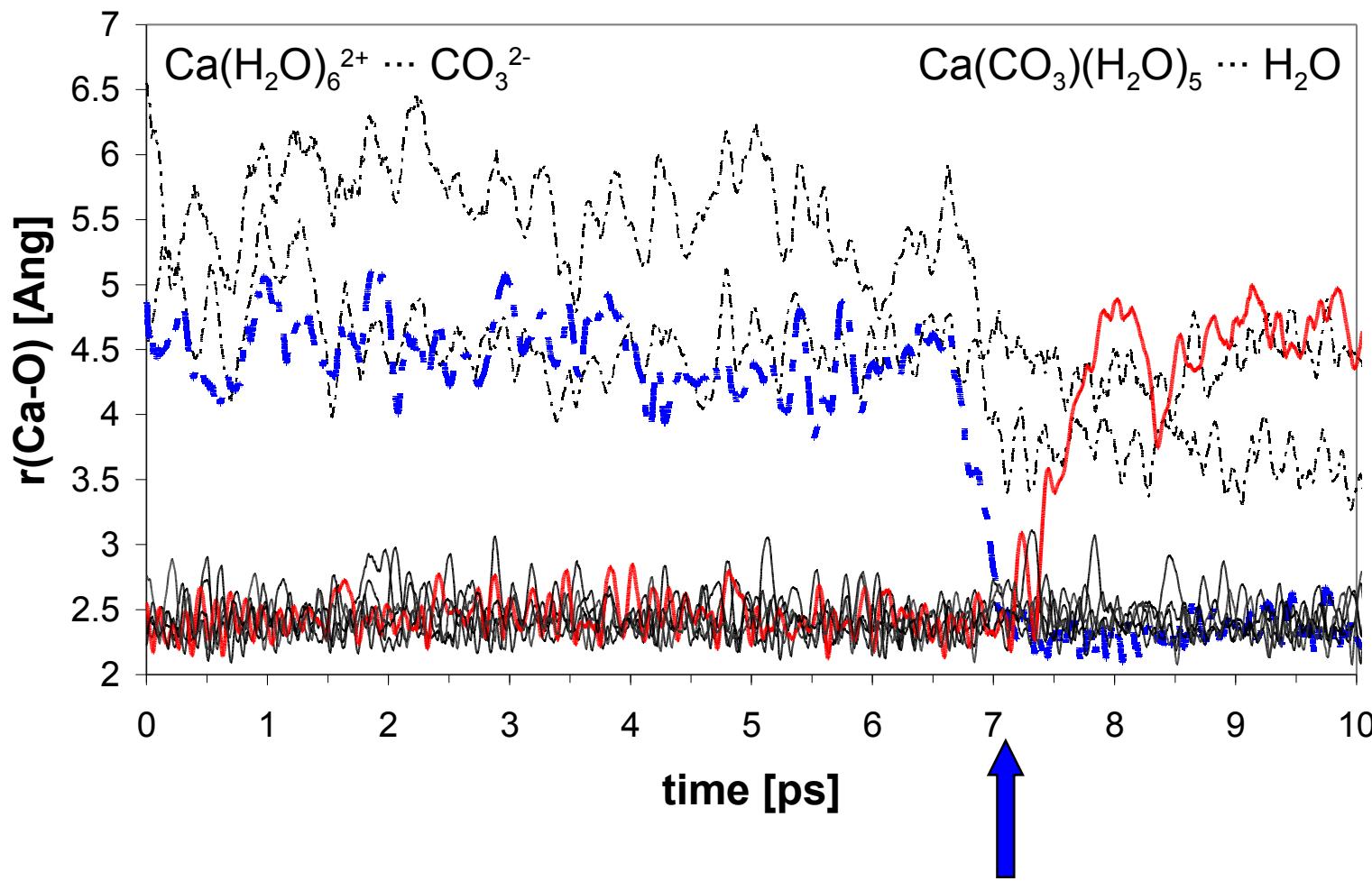
Snapshots from CPMD simulation.

$\text{Ca}^{2+}, \text{CO}_3^{2-}$ in 52 H_2O molecules

The formation of the *monomer* of CaCO_3 occurs with an
associative mechanism

D. Di Tommaso and N. H. de Leeuw,
J. Phys. Chem. B **112**, 6965 (2008).

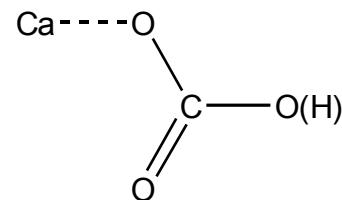
Formation of the monomer of CaCO_3



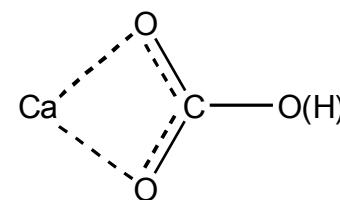
Time evolution of Ca–O distance during CPMD simulation.

Structural properties of CaCO_3 in aqueous solution

- Coordination mode of CO_3^{2-} and HCO_3^- to Ca^{2+} ?

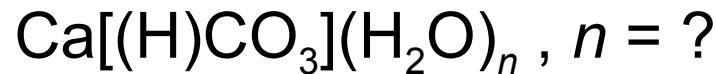


monodentate (η^1)

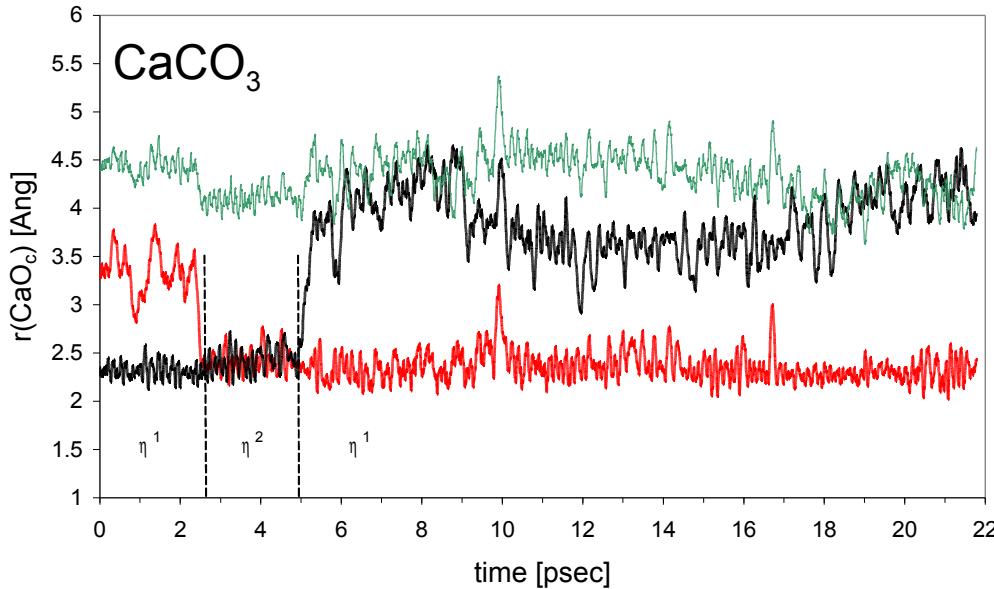


bidentate (η^2)

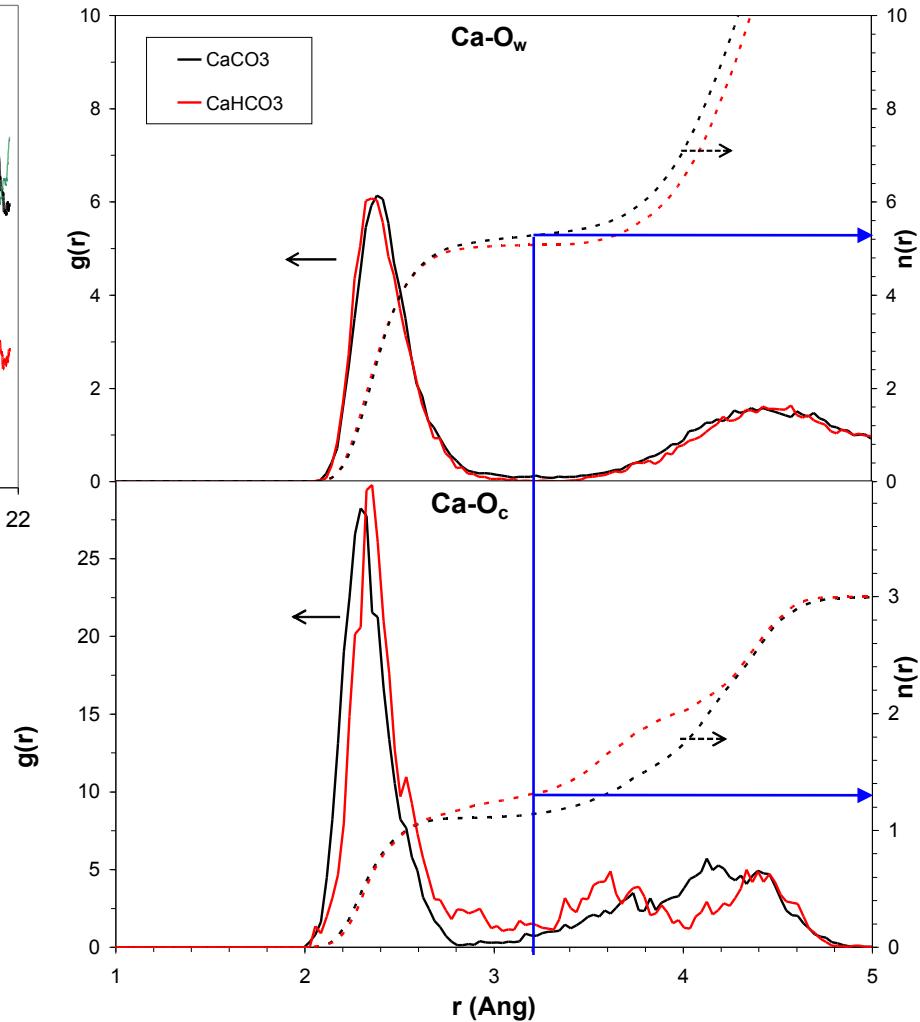
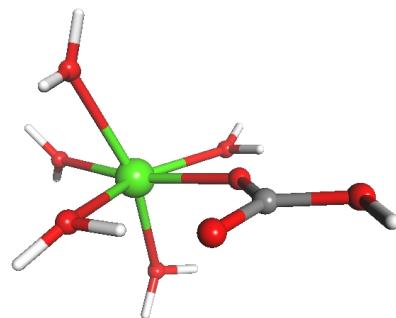
- First hydration shell of Ca^{2+} ?



Structural properties of CaCO_3 in aqueous solution



Building block of $\text{Ca}(\text{H})\text{CO}_3^{(+)}$ in sol



Static *ab initio* simulations

DMol³ code [B. Delley, *J. Chem. Phys.* **113**, 7756 (2000)].

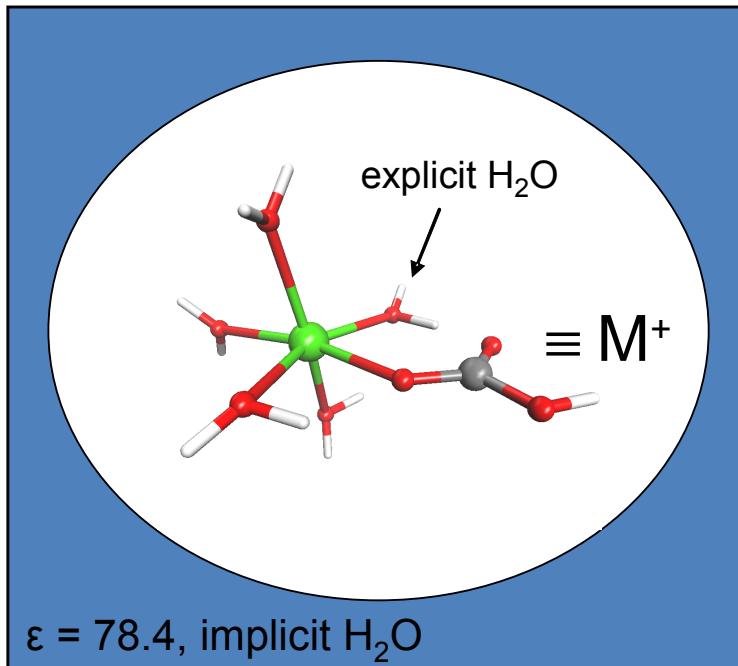
- Double-numeric-polarized (DNP) basis sets
- PBE approximation for E_{xc}
- COSMO to model the solvent as a dielectric continuum

Gaussian code [M.. J. Frisch *et al.*, Gaussian, Inc., Wallingford CT, 2004].

- aug-cc-pVTZ Gaussian basis sets
- mPW1B95 approximation for E_{xc}
- UAHF/CPCM solvation model

Oligomerization of calcium bicarbonate species

Hybrid microsolvation cluster/continuum approach

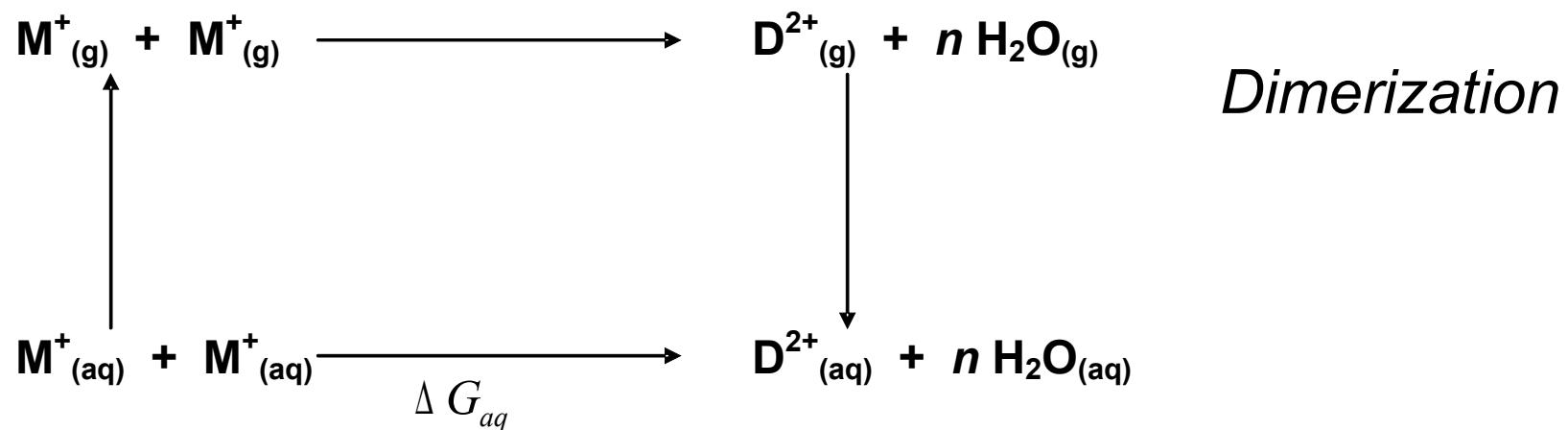


Condensation reactions in aqueous solution:

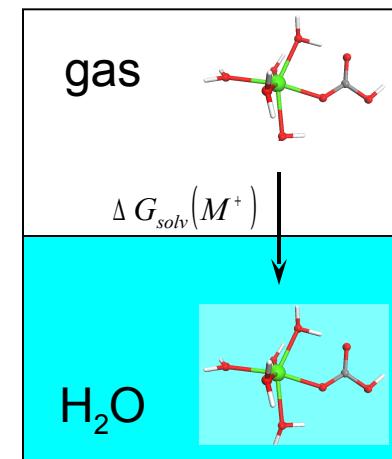


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Oligomerization of calcium bicarbonate species

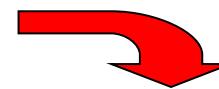


$$\begin{aligned}
 \Delta G_{aq} &= \Delta G_{gas} + \Delta \Delta G_{solv} \\
 \Delta G_{gas} &= \sum G_{gas}(prod) - \sum G_{gas}(react) \\
 \Delta \Delta G_{solv} &= \sum \Delta G_{solv}(prod) - \sum \Delta G_{solv}(react)
 \end{aligned}$$



Dimerization of calcium bicarbonate species

Reactions	ΔG_{gas}	$\Delta \Delta G_{solv}$	ΔG_{aq}
$M^+ + M^+ \rightarrow D1 + 2 H_3O^+$	142.0	-110.5	31.5
$M^+ + M^+ \rightarrow D1^+ + H_2O + H_3O^+$	51.3	-39.2	12.1
$M^+ + M^+ \rightarrow D1^{2+} + 2 H_2O$	24.6	-12.6	12.0
$M^+ + M^+ \rightarrow D2^{2+} + H_2O$	43.7	-30.9	12.7
$M^+ + M^+ \rightarrow D3^{2+} + H_2O$	22.2	-19.7	2.5
$M^+ + M^+ \rightarrow D4^+ + H_3O^+$	45.3	-40.0	15.3
$M^+ + M^+ \rightarrow D4^{2+} + H_2O$	21.8	-10.4	11.2
$M^+ + HCO_3^- \rightarrow Ca(HCO_3)_2(H_2O)_4 + H_2O$	-106	115.9	9.9
$Ca(HCO_3)_2(H_2O)_4 + HCO_3^- \rightarrow Ca(HCO_3)_3(H_2O)_3^- + H_2O$	-36.2	34.8	6.0



The dimerization is endo-ergonic

ΔG_{gas} computed at the mPW1B95/aug-cc-pVTZ level of theory.

$\Delta \Delta G_{solv}$ evaluated using the UAHF/CPCM solvation model at the HF/6-31G(d) level of theory.

Conclusions

- Complementary first principle simulations to study the formation, hydration structure, stability, and oligomerization of $\text{Ca}(\text{H})\text{CO}_3$ species.
- The formation of the CaCO_3 *monomer* in aqueous solution is an **associative mechanism**.
- The dominant building block of calcium (bi-)carbonate in aqueous solution is $\text{Ca}[\eta^1-(\text{H})\text{CO}_3](\text{H}_2\text{O})_5^+$.
- The oligomerization of calcium bicarbonate species in water is **endo-ergonic** at the conditions of $T = 298 \text{ K}$ and neutral pH.

Acknowledgements



Prof. N. H. de Leeuw

Dr. A. Tilocca



MARIE CURIE **ACTIONS**



Engineering and Physical Sciences
Research Council

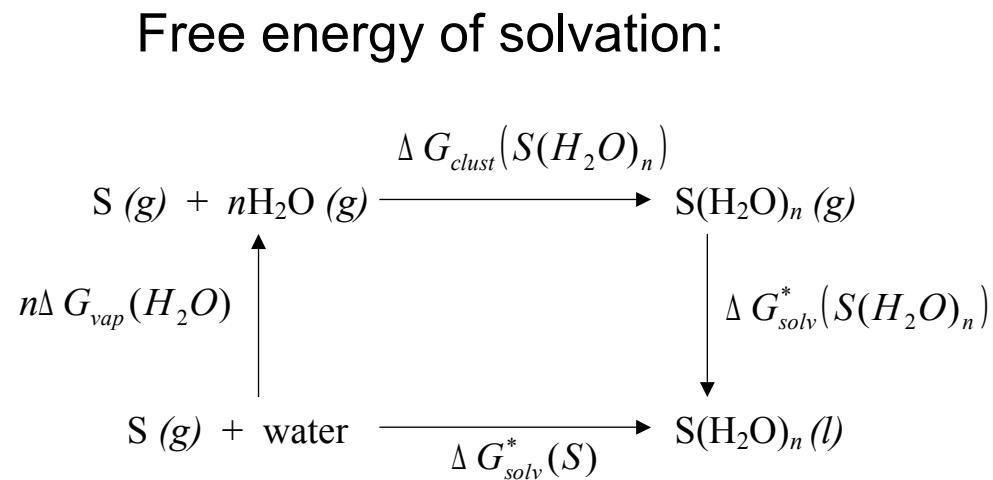
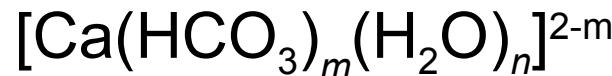
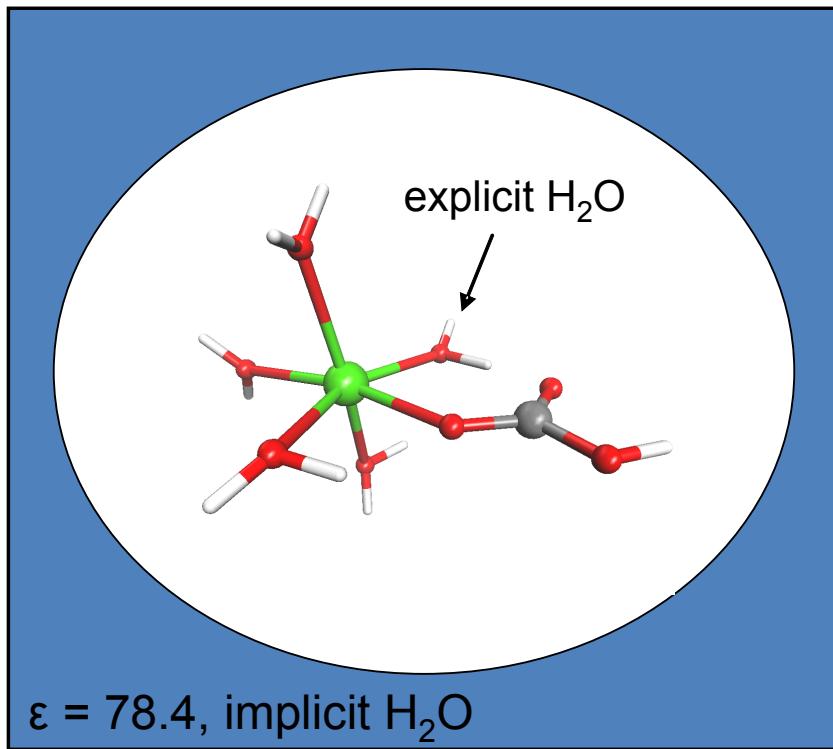


HPCx and HECToR resources -
Material Chemistry Consortium

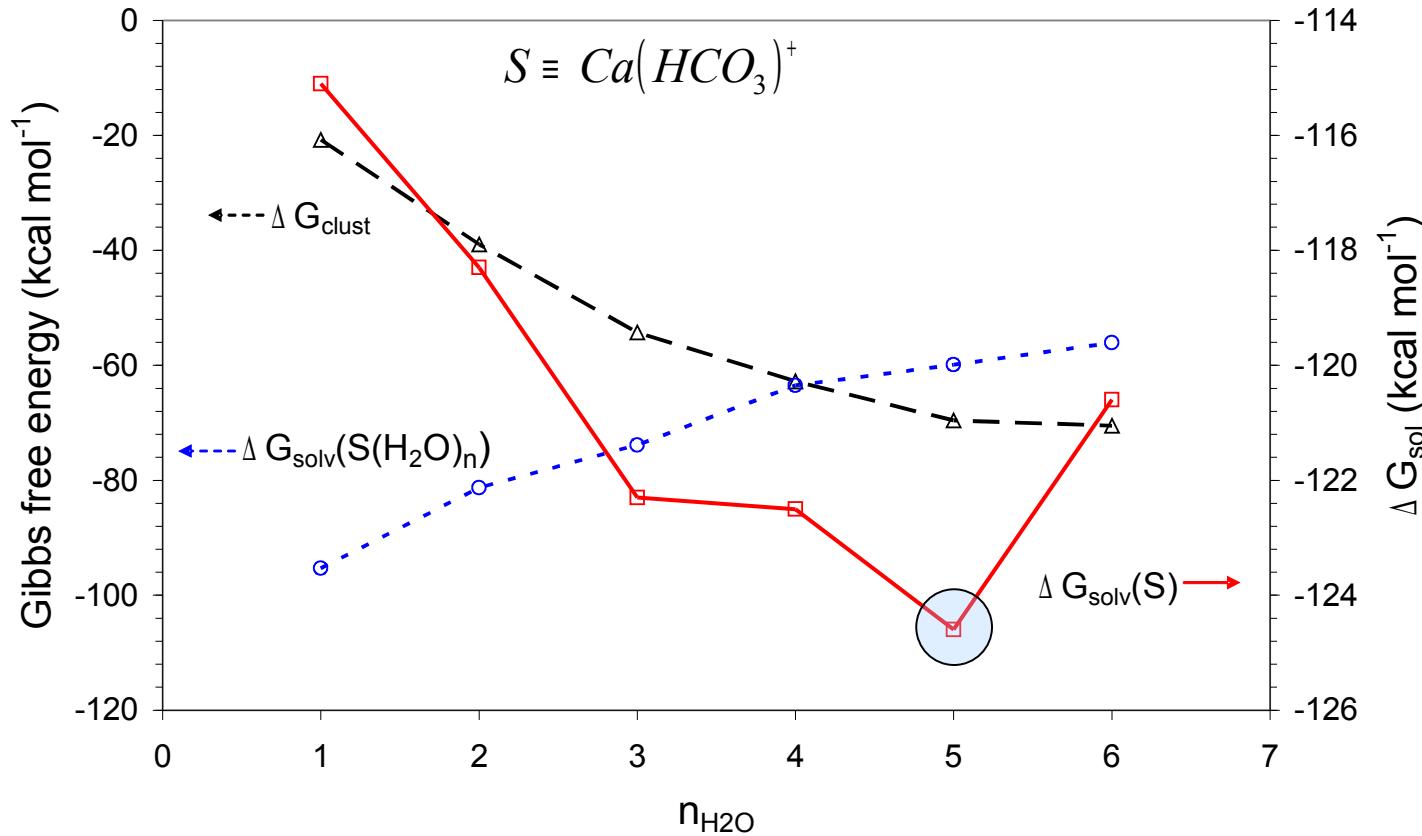


Speciation in aqueous calcium bicarbonate

Hybrid Microsolvation/Continuum approach



$$\Delta G_{solv}^*(S) = \Delta G_{clust}(S(H_2O)_n) + \Delta G_{solv}^*(S(H_2O)_n) + n\Delta G_{vap}(H_2O)$$



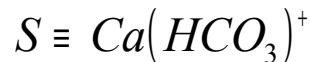
Solvation free energy of $Ca(HCO_3)^+$ computed at the PBE/DNP – COSMO level.



most stable hydrated $Ca(HCO_3)^+$ species: $Ca[\eta^1-HCO_3](H_2O)_5^+$

Speciation in aqueous calcium bicarbonate

$$\Delta G_{solv}^*(S) = \Delta G_{clust}(S(H_2O)_n) + \Delta G_{solv}^*(S(H_2O)_n) + n\Delta G_{vap}(H_2O)$$



Species	$n\Delta G_{vap}(H_2O)$	$\Delta G_{clust}(S(H_2O)_n)$	$\Delta G_{solv}^*(S(H_2O)_n)$	$\Delta G_{solv}^*(S)$
$Ca(\eta^2-HCO_3)^+$			-111.4	-111.4
$Ca(\eta^2-HCO_3)(H_2O)^+$	1.0	-20.8	-95.3	-115.1
$Ca(\eta^2-HCO_3)(H_2O)_2^+$	2.0	-39.0	-81.3	-118.3
$Ca(\eta^2-HCO_3)(H_2O)_3^+$	3.0	-54.3	-69.5	-120.8
$Ca(\eta^1-HCO_3)(H_2O)_3^+$	3.0	-48.2	-73.9	-122.3
$Ca(\eta^2-HCO_3)(H_2O)_4^+$	4.0	-62.8	-63.5	-122.3
$Ca(\eta^1-HCO_3)(H_2O)_4^+$	4.0	-62.0	-64.5	-122.5
$Ca(\eta^2-HCO_3)(H_2O)_5^+$	5.0	-69.4	-59.0	-123.4
$Ca(\eta^1-HCO_3)(H_2O)_5^+$	5.0	-69.6	-59.9	-124.6
$Ca(\eta^1-HCO_3)(H_2O)_6^+$	6.0	-70.5	-56.1	-120.6



Solvation free energies computed at the PBE/DNP – COSMO level (in kcal/mol).

Speciation in aqueous calcium bicarbonate

$$\Delta G_{solv}^*(S) = \Delta G_{clust}(S(H_2O)_n) + \Delta G_{solv}^*(S(H_2O)_n) + n\Delta G_{vap}(H_2O)$$

Species	$n\Delta G_{vap}(H_2O)$	ΔG_{clust}	$\Delta G_{solv}^*(S(H_2O)_n)$	$\Delta G_{solv}^*(S)$
$Ca(HCO_3)_2$			-31.8	-31.8
$Ca(HCO_3)_2(H_2O)$	1.0	-7.3	-25.8	-32.2
$Ca(HCO_3)_2(H_2O)_2$	2.0	-12.1	-24.7	-33.1
$Ca(HCO_3)_2(H_2O)_3$	3.0	-10.3	-25.8	-33.1
$Ca(HCO_3)_2(H_2O)_4$	4.0	-15.4	-23.7	-35.1
$Ca(HCO_3)_3^-$			-58.6	-58.6
$Ca(HCO_3)_3(H_2O)^-$	1.0	0.2	-58.6	-57.4
$Ca(HCO_3)_3(H_2O)_2^-$	2.0	-5.4	-58.4	-61.8
$Ca(HCO_3)_3(H_2O)_3^-$	3.0	23.0	-61.5	-35.5

Solvation free energies computed at the PBE/DNP – COSMO level (in kcal/mol).