Molecular features of the air/carbonate solution interface

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Introduction

The nature of the air/carbonate solution interface study

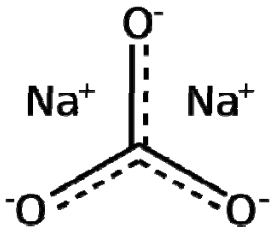
The experiment (air/solution interfacial water structures)

→ sum-frequency vibrational spectroscopy(SFVS)

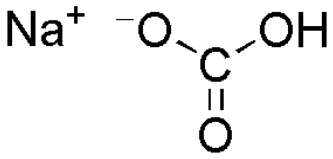
The theory → molecular dynamics simulations (MDS).

Sample

Saturated sodium bicarbonate(1.1 M) and
sodium carbonate(2.3 M) solutions in water at 23 ◦C



sodium carbonate



sodium bicarbonate

MD simulation

The AMBER 9 simulation program package

Simulation box parameters and particle numbers

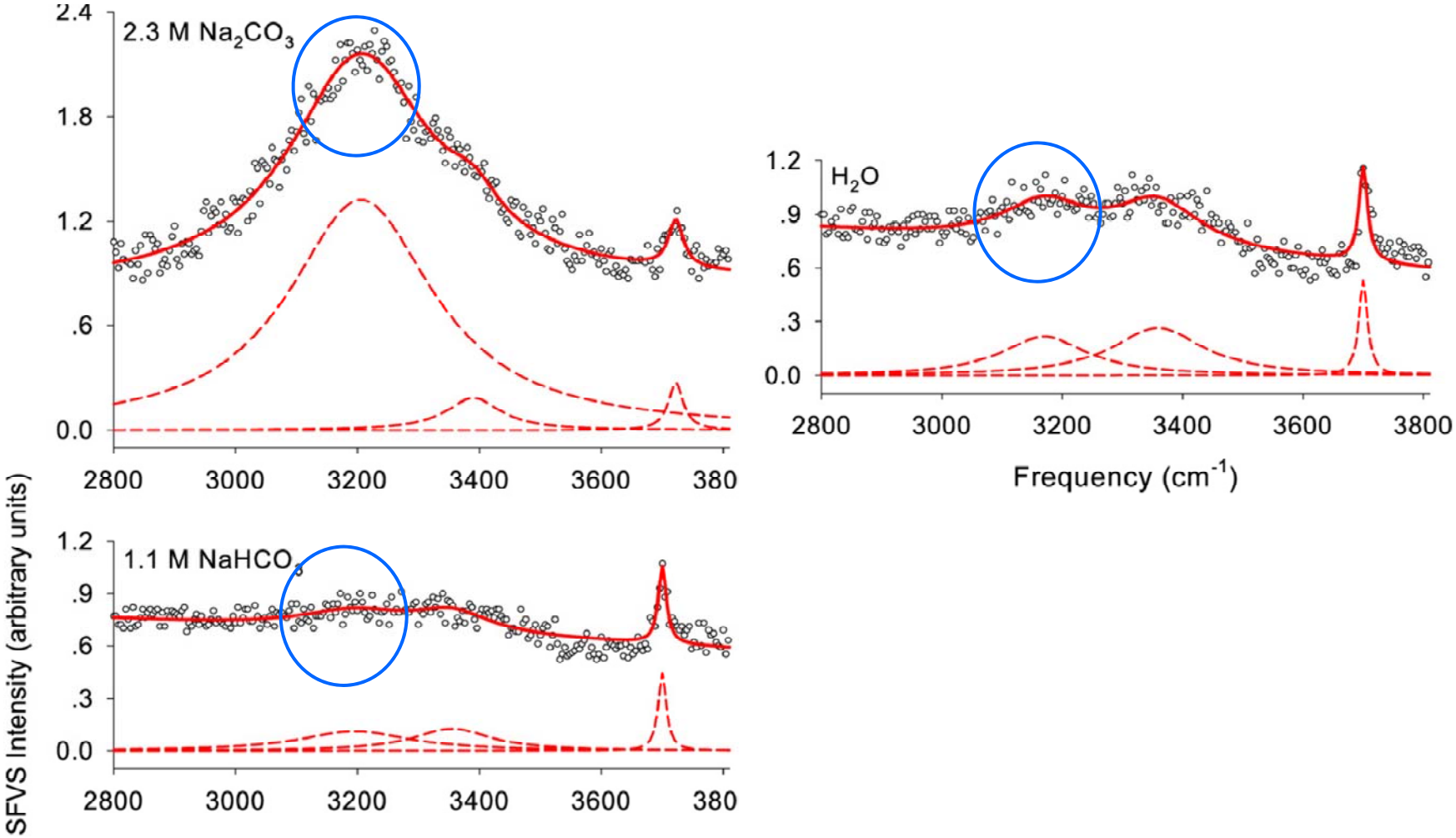
	Cell size (Å) ($X \times Y \times Z$)	Number of cations	Number of anions	Number of water molecules	Concentration (M)
Na_2CO_3	$27.5 \times 25 \times 100$	50	25	691	2.0
$NaHCO_3$	$26.5 \times 28.5 \times 100$	20	20	1016	1.1

Parameters of non-bonded interactions for sodium carbonate and sodium bicarbonate salts

Salt	Atoms	Charge (e)	α_i (Å)	ε_i (kcal/mol)	Polarizability [25]
Na_2CO_3	Na [32]	1.0000	2.8760	0.1000	0.250
	C [33]	0.6052	3.1256	0.0576	0.616
	O [33]	−0.8684	3.5532	0.1554	0.434
NaHCO3	Na [32]	1.0000	2.8760	0.1000	0.250
	C [33]	0.8100	3.1256	0.0576	0.616
	O [33]	−0.7500	3.5532	0.1554	0.434
	Hydroxyl oxygen	−0.7200	3.5532	0.1554	0.465
	Hydroxyl hydrogen	0.4100	n/a	n/a	0.135

Results and discussion

1. SFVS spectra at an air/solution interface



2. Molecular dynamics simulation

2.1. Ion distribution at air/solution interface

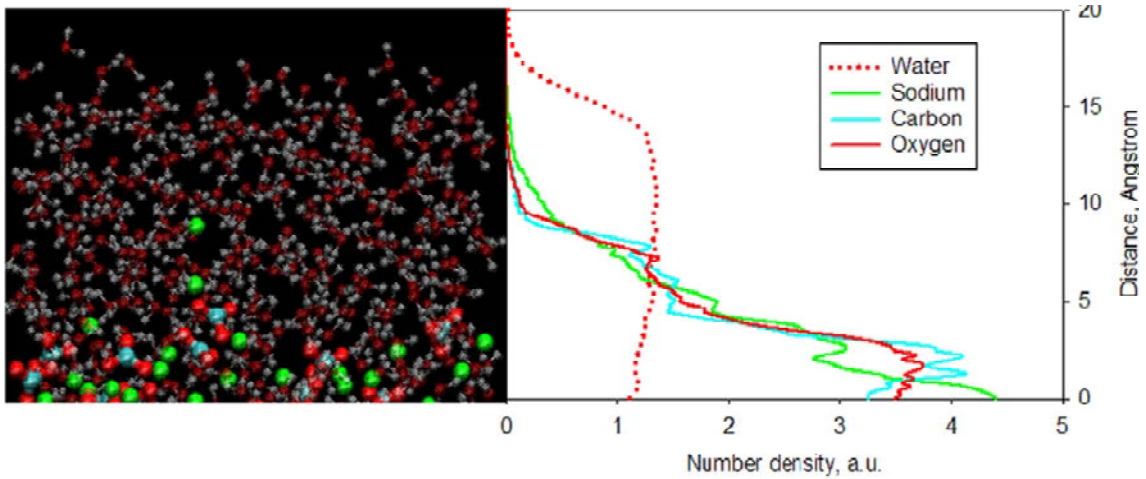


Fig. 2. Snapshot of aqueous sodium carbonate solution (2.0 M) (left) and particle number density distributions along surface normal (right). The color representations are as follow: Cyan—carbon, green—sodium, red—oxygen, and white—hydrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

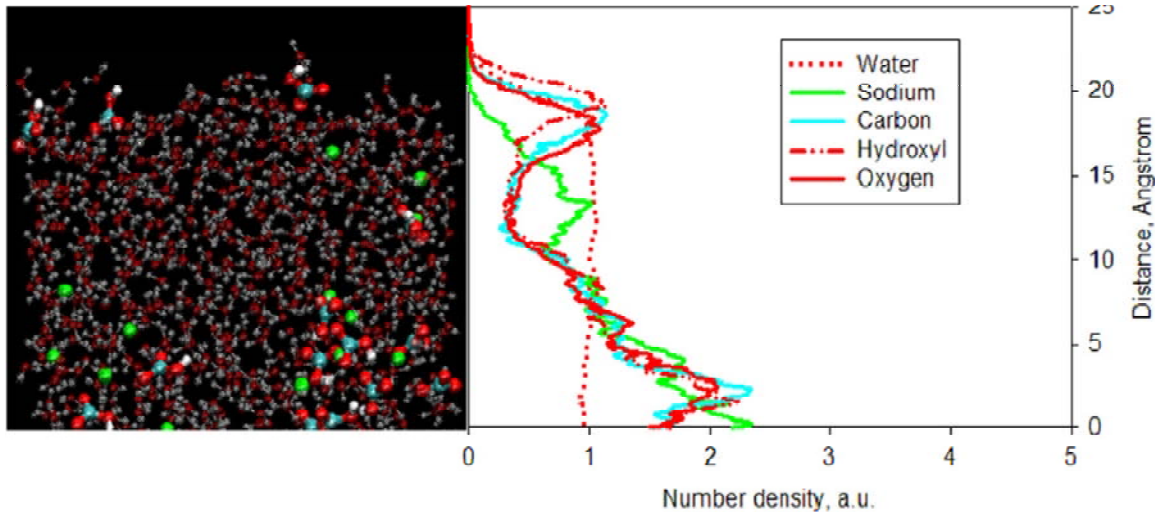


Fig. 3. Snapshot of aqueous sodium bicarbonate solution (1.1 M) (left) and particle number density distributions along surface normal (right). The color representations are as follow: Cyan—carbon, green—sodium, red—oxygen, and white—hydrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Solution surface tension calculation

$$\gamma = \frac{1}{2} L_z \left\langle P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right\rangle$$

where L_z is the length of the simulation box in the z direction and P_{ii} ($i = x$, y, and z) is the diagonal components of the pressure tensor.

Table 3
Comparison of simulation and experimental results for the increase in surface tension relative to pure water

Salt	Concentration (M)	Surface tension change (mN/m)	
		MDS calculation	Experimental measurement [11]
Na_2CO_3	2.0	5.6 ± 0.6	3.8
$NaHCO_3$	1.1	2.0 ± 1.0	0.8

water dipole moments density distribution

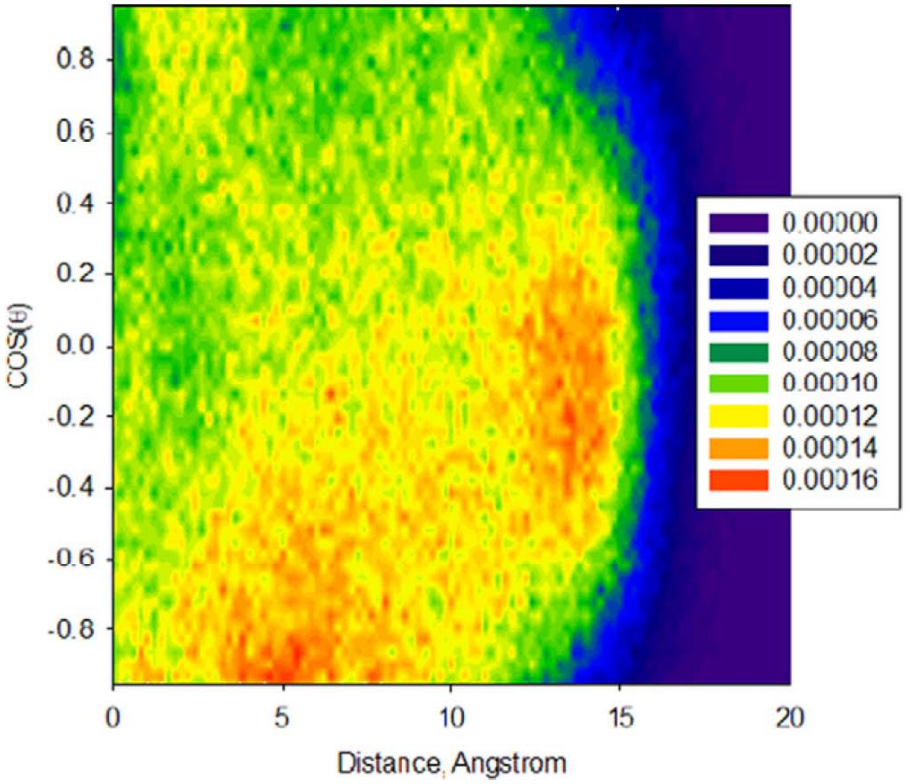


Fig. 4. Water dipole moment density distribution along sodium carbonate solution air/solution surface normal. The color bar in the legend box represents relatively density (angle q: the angle between the water dipole moment and air/solution surface normal).

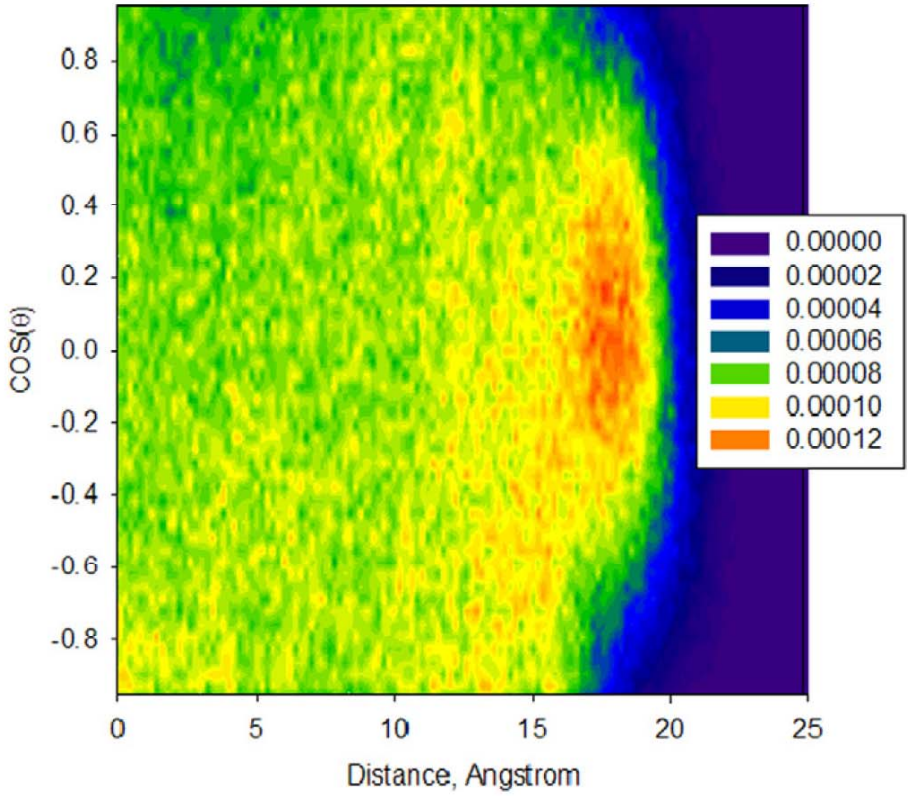


Fig. 5. Water dipole moment density distribution along sodium bicarbonate solution air/solution surface normal. The color bar in the legend box represents relatively density (angle q: the angle between the water dipole moment and air/solution surface normal).

Water dipole moment distribution and SFVS

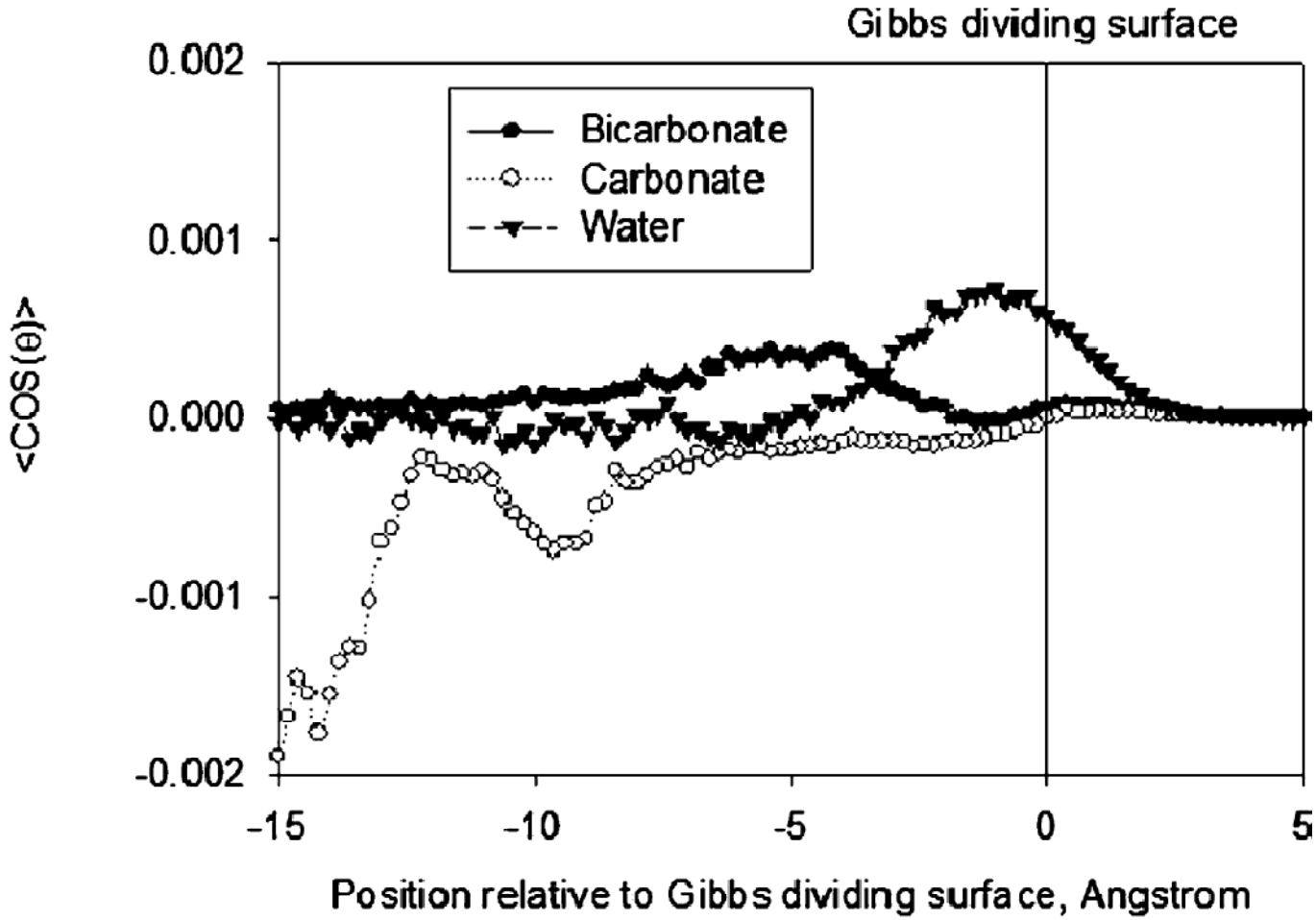


Fig. 6. Average water dipole moment as a function of location in the sodium carbonate, sodium bicarbonate, and pure water solutions from MD simulations. (The Gibbs dividing surface is defined as the position where water density is equal to one-half its bulk density.)

Conclusions

Due to the strong hydration of the carbonate ions in the solution, negative surface adsorption has been observed from MDS

Expansion of the interfacial layer thickness contributes to enhance the SFVS water signals.

Carbonate ions show obvious structural making characteristics

Bicarbonate ions show obvious structural breaking characteristics