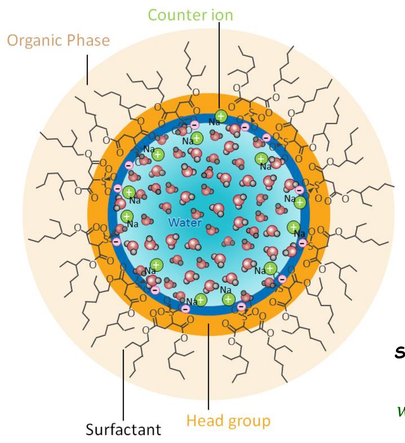
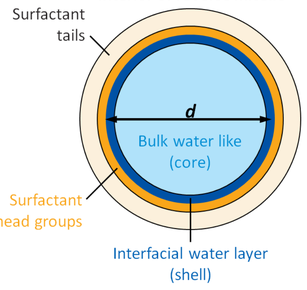
Spectroscopic Approach for Nanoconfined Water Structure via Core/Shell Model

Jooyong Lee[†,‡], Jonggu Jeon[†,‡], Min-Seok Kim[†,‡], Kyungwon Kwak[*,§] and Minhaeng Cho[*,†,‡]

[†]Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Department of Chemistry, Korea University, Seoul 136-701, Republic of Korea
[‡]Department of Chemistry, Korea University, Seoul 136-701, Republic of Korea
[§]Department of Chemistry, Chung-Ang University, Seoul 156-756, Republic of Korea

❖ Interior of Reverse Micelle





Size Determination of reverse micelle

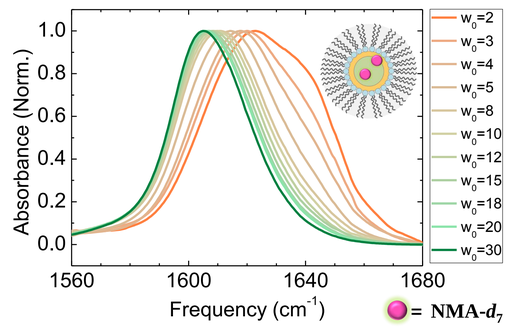
$$w_o = \frac{[H_2O]}{[AOT]} \qquad d_{wp} = 0.29W_o + 1.1\ (nm)$$

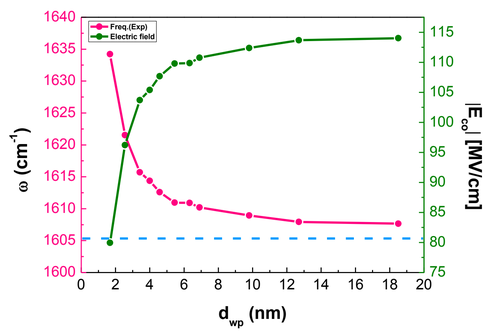
w_0	d_{wp} (nm)	V_{wp} (10^{-27})	# of H_2O	# of Solute*
2	1.68	2.482713	82.99008	0.747545
5	2.55	8.681988	290.2144	2.614146
8	3.42	20.94483	700.1268	6.30649
10	4	33.51032	1120.156	10.08996
12	4.58	50.30314	1681.492	15.14627
15	5.45	84.75945	2833.269	25.52107
18	6.32	132.1752	4418.243	39.79794
20	6.9	172.0069	5749.706	51.79128
30	9.8	492.807	16473.15	148.3842
40	12.7	1072.531	35851.68	322.939

* Solute : 1) NMA-d_7 2) HN_3

❖ Electrostatic Environment in RMs

(*Pure Appl. Chem.* 2014, *86*, 135-149)





Solvent Electric Field $|E_{co}|$ at the CO group of NMA-d_7

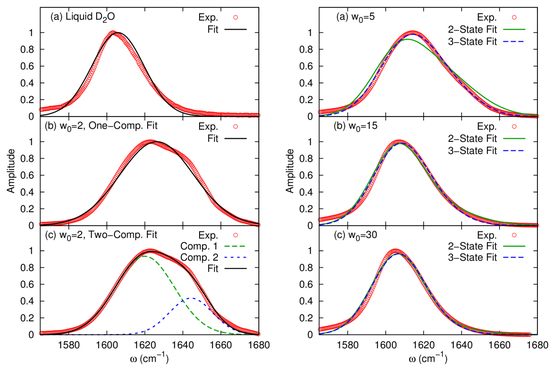
$$|\mathbf{E}_{CO}| = |\phi_C - \phi_O|/r_{CO} = \left|\frac{\Delta\omega}{l' r_{CO}}\right|$$

- ✓ Amide I' vibrational frequency shift due to chromophore-solvent electrostatic interactions
- ✓ When combined with electric potential due to solvent partial charges extracted from MD trajectories, this method can quantitatively predict the solvatochromic frequency shifts of amide modes of NMA in AOT RM.

❖ Theoretical Background of Two-/Three-Ensemble model

(J. Lee et al. *Pure Appl. Chem.* 2014, *86*, 135-149)

Employment of Subensemble Model



- ✓ A small population of a third state (termed "shell-2" state above) with even weaker intermolecular interaction was also found in small RMs, but its existence does not markedly change the two-state picture.

MD Simulations

Molecular mechanics (MM) force field

Isooctane: TraPPE united atom force field (No explicit hydrogen)
AOT anion: Hybrid TraPPE (carbon tail) and CGenFF 2b7 (head group)
Water: Rigid TIP4P model
Na^+: CHARMM or Jensen-Jorgensen
NMA-d_7: CHARMM

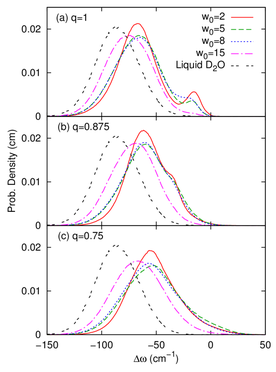
CHARMM and NAMD packages are used for system build-up and NAMD is used for MD.

All bonds involving H/D are constrained.
2 fs time step size
Periodic boundary condition and particle mesh Ewald (PME) electrostatics.
Lennard-Jones interactions are cut off at 12 Å.

To maintain spherical micelle structure, harmonic restraints are applied on surfactant sulfur atoms during equilibration of more than 10 ns.
In production runs of 1.5-2 ns, only water and Na^+ are weakly restrained within a sphere.

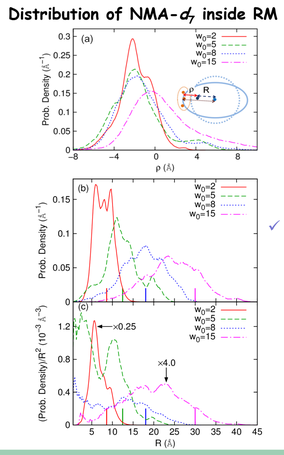
Configurations were saved every 0.05 ps for FFCF calculation.

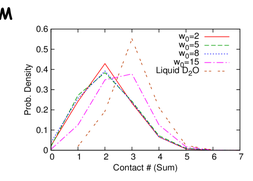
Computational Results



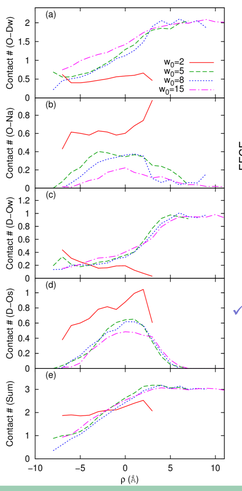
- ✓ The "shell-2" state is small number of interfacial NMA-d_7 has a spectator Na^+ ion located around its amide H.

Distribution of NMA-d_7 inside RM

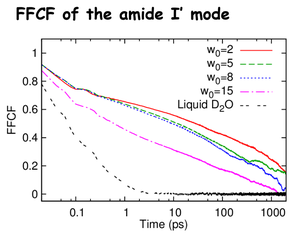




- ✓ Since the frequency begins to deviate from the bulk liquid value only at **ρ<~4 Å**, this distance can be regarded as the boundary of the core and shell regions of the water phase.



FFCF of the amide I' mode

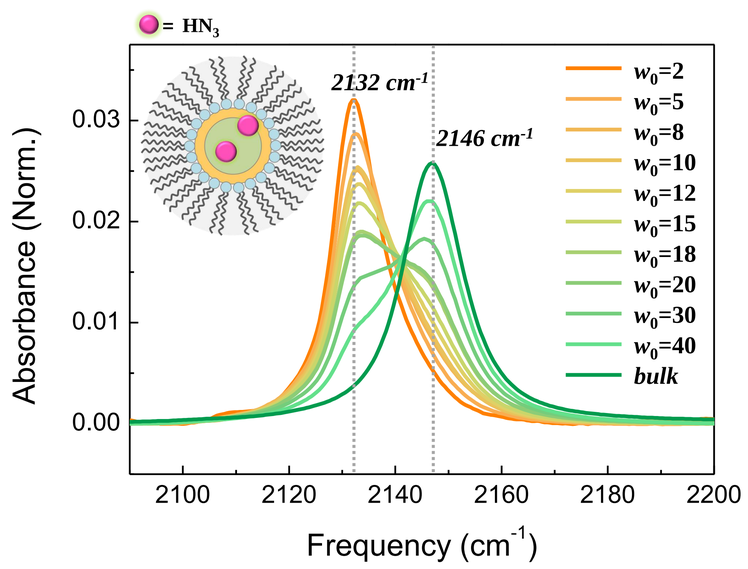


- ✓ These vastly different time scales would have significant consequences on the motional narrowing of IR linewidths.

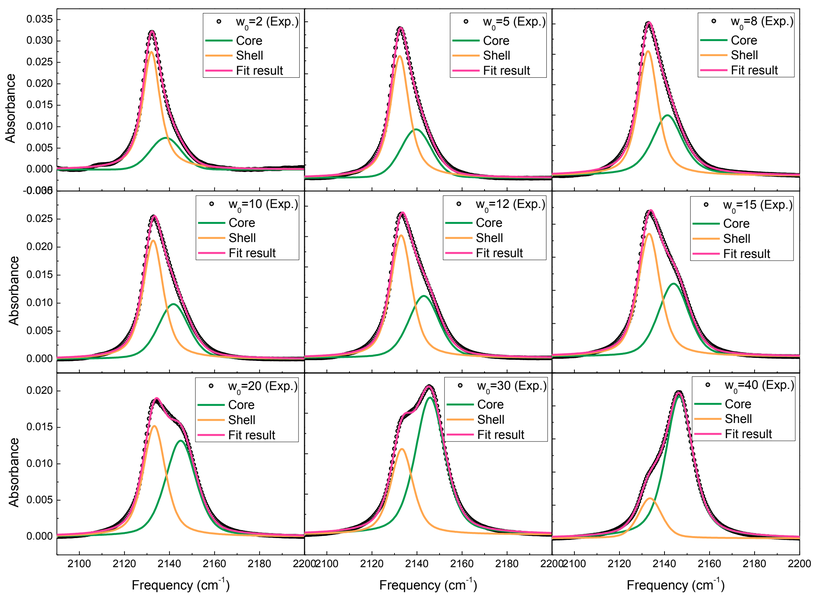
❖ Simple Two-Ensemble model

(J. Lee et al. *J. Phys. Chem. Lett.* 2014, *5*, 3404-3407)

FT-IR Spectroscopy



$$A_{total}(\omega) = A_{core}(\omega) + A_{shell}(\omega)$$

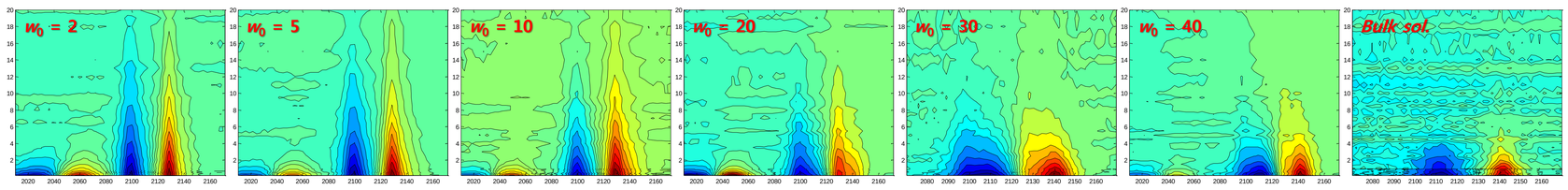


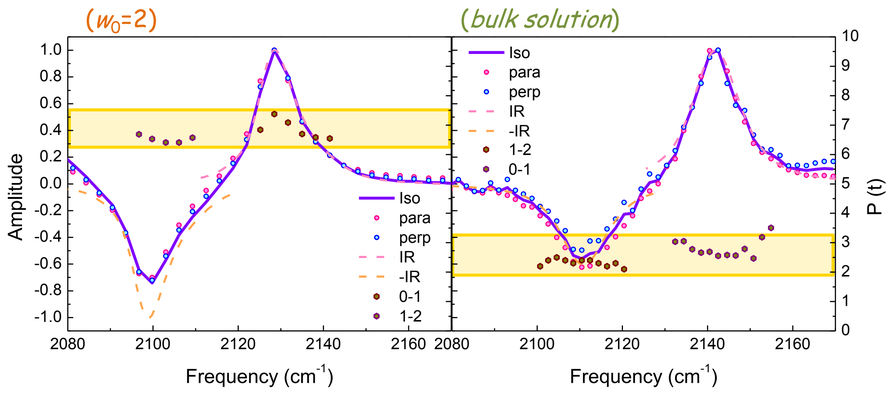
- ✓ The hydrazoic acid has been found to possess most of important characteristics of good IR probes for studying water structures in nanoconfined environment.
- ✓ The spectral components commonly referred to as core and shell are well-separated and easily identified in the infrared absorption spectra.

❖ Expansion of Two-Ensemble(Core/Shell) Model

(J. Lee et al. *J. Phys. Chem. Lett.* 2014, *5*, 3404-3407)

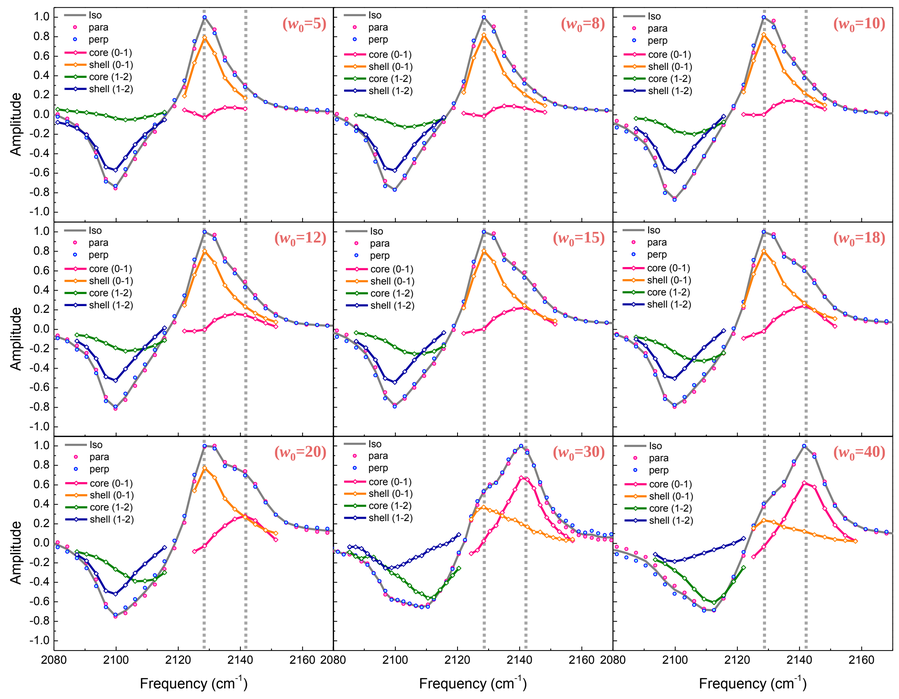
IR Pump-Probe Spectroscopy

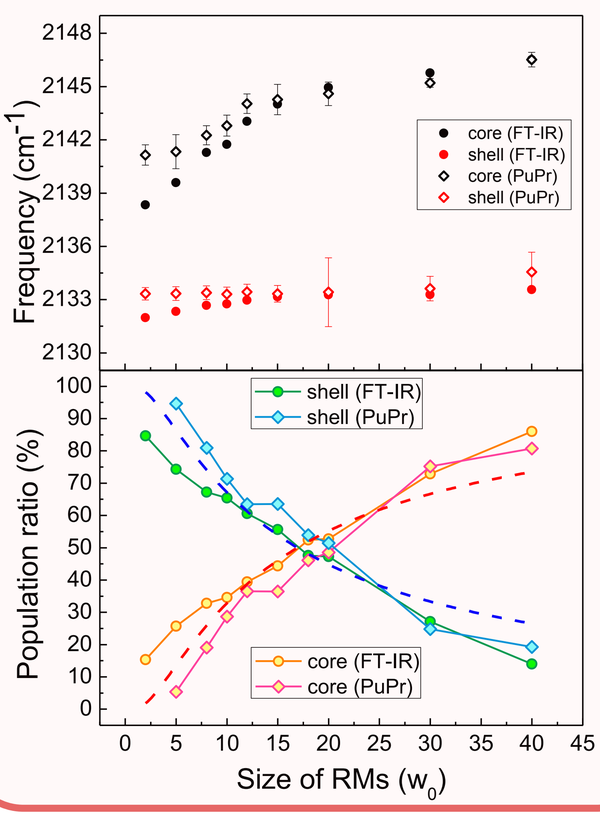




➡ Life time of shell area : **6.479 (ps)** ➡ Life time of core area : **2.318 (ps)**

$$C(t) = A_{core}e^{-t/T_{core}} + A_{shell}e^{-t/T_{shell}}$$





- ✓ The polarization-controlled IR pump-probe spectroscopy revealed that the vibrational relaxation process of HN_3 molecules in the shell part occurs on much slower time scale, indicating weak or no H-bonding interaction with water molecules. Furthermore, the vibrational lifetime of the HN_3 molecules in the core region shows a weak dependence on RM size. The present work therefore supports the simple core-shell model, and the H-bonding environment around the IR probe is significantly different for the two regions. It is believed that despite the notable influence of the nanoconfinement on the water H-bond network structure local interaction of water molecules with the probe remains relatively unchanged.