Water can vitrify on the nanoscale at ambient conditions

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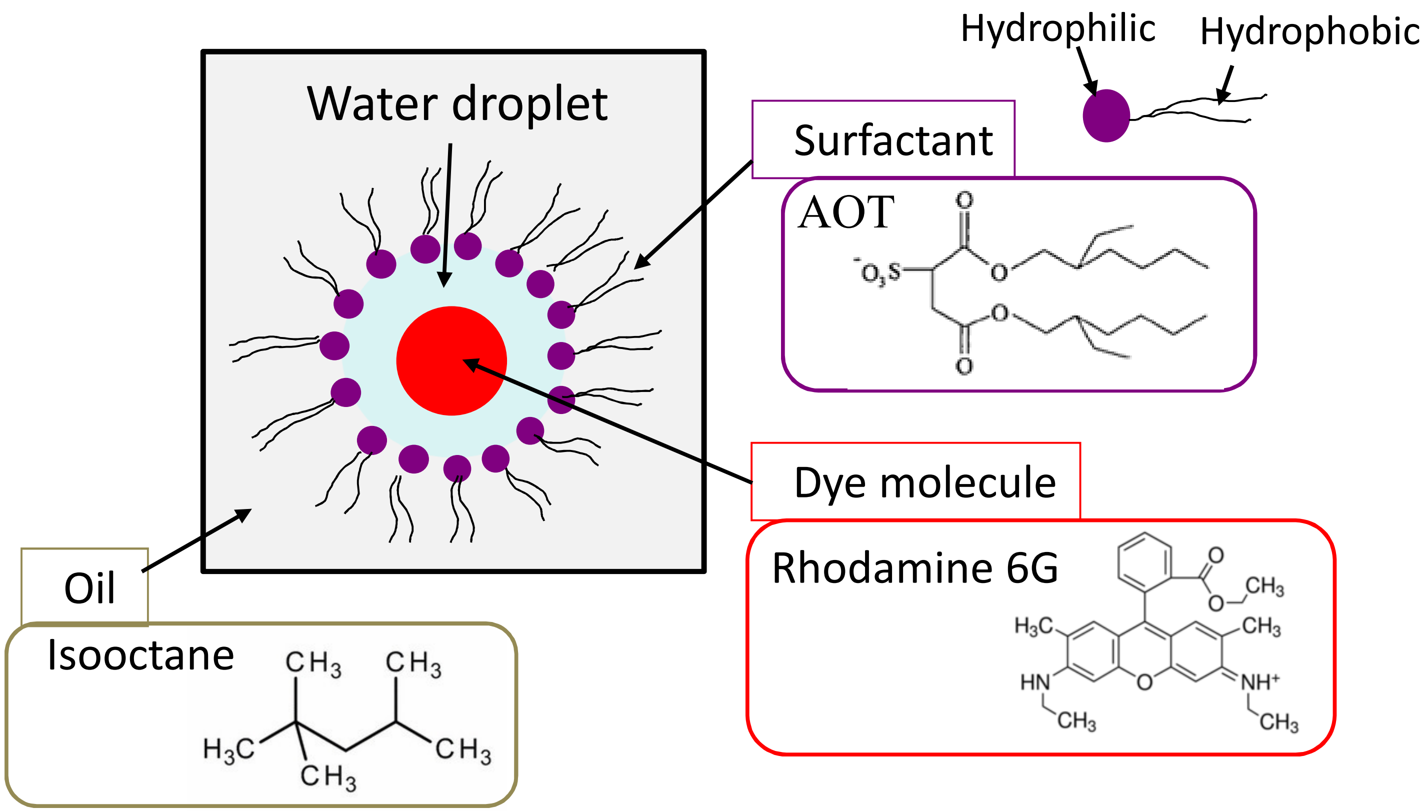
Abstract

- Nanoconfined water is ubiquitous at ambient conditions naturally and industrially.
  (, although it is often used for studies of supercooled water at low temperatures)
- An important question is how its dynamic behavior changes owing to the confinement, because it is crucial for properties of systems where nanoconfined water resides.
- We conducted hole-burning spectroscopy of probe molecules (rhodamine 6G) within AOT/isooctane reverse micelles at the water-droplet sizes from ~1.6 nm to ~7 nm
- The result demonstrate that the water changes from a liquid to glass state at ~4 nm, that is, shows a liquid-glass transition owing to the confinement.
- Surprisingly, nanoconfined water exhibits slowing down by over 12 orders of magnitude in time and increase in the transition temperature by over 150 degrees compared with bulk water.
- Our findings for soft matter suggest that water can vitrify on a nanoscale locally in cytoplasm with molecular crowding and glassy behaviors.

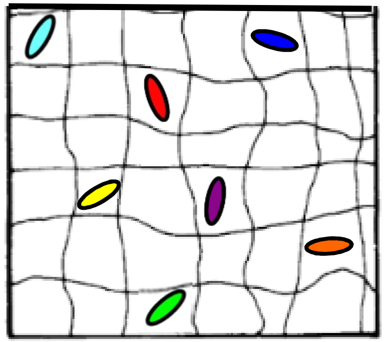
Nanoscale confinement of water using reverse micelle [1]



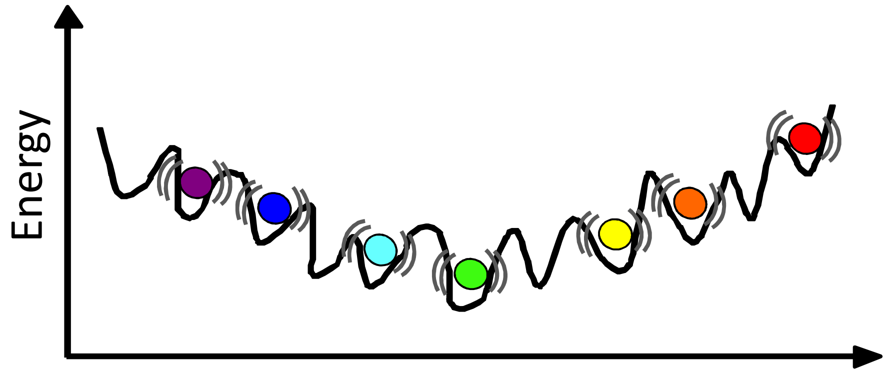
- We introduce a hydrophilic dye molecule for probing the (liquid or glassy) state of water.
- We control the droplet size for examining how the state changes with the droplet size

[1] Murakami et al. J. Phys. Chem. B (2011); Phys. Rev. E (2013); J. Chem. Phys. (2018).

Dye molecules (as a probe)
in a glassy system

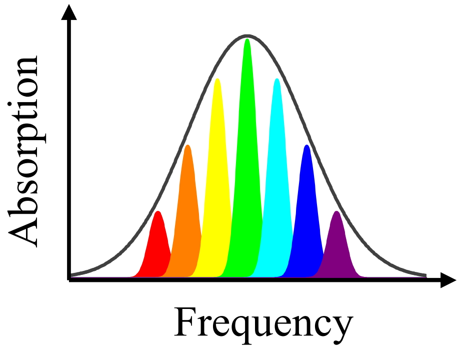


Electronic ground state of the dye molecule
～ Many local mimima



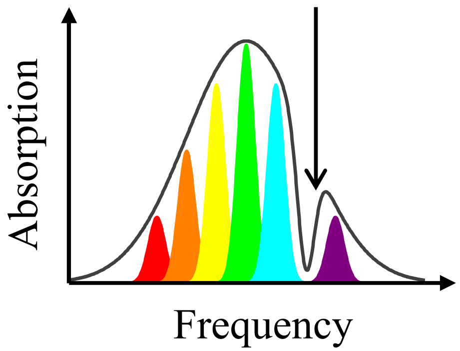
In a glassy state of the surroundings, the dye molecules are trapped in the local minima, and have different electronic transition frequencies (colors).

If the surroundings of the dye molecule are in a glassy state (on a laboratory time scale, several minutes here), HB spectrum shows a spectral shift depending on excitation frequency.

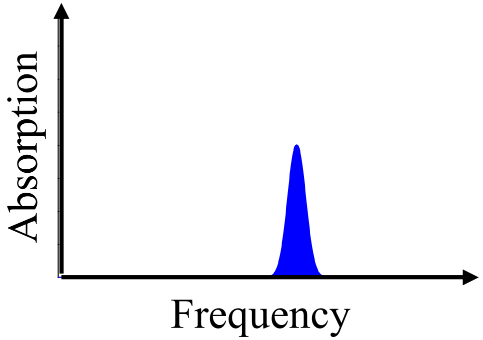


A sum of absorption spectra of dye molecules at each site

Hole-burning (HB)

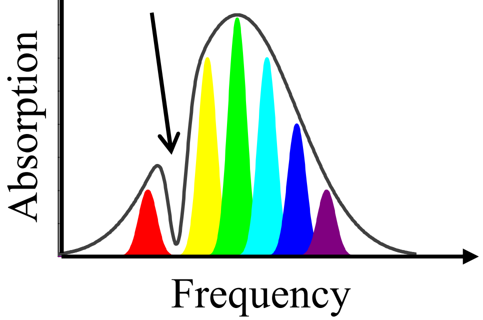


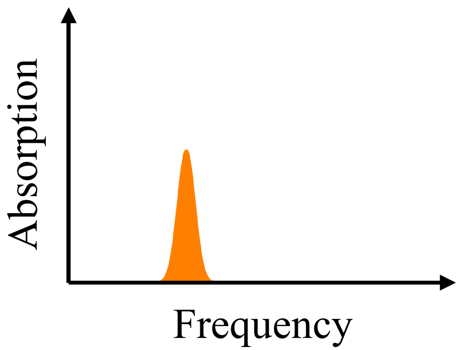
HB spectrum



Laser excitation
at different frequencies

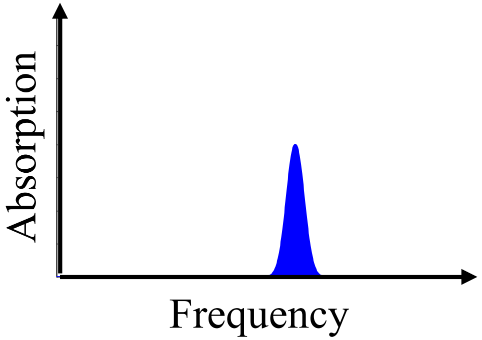
HB

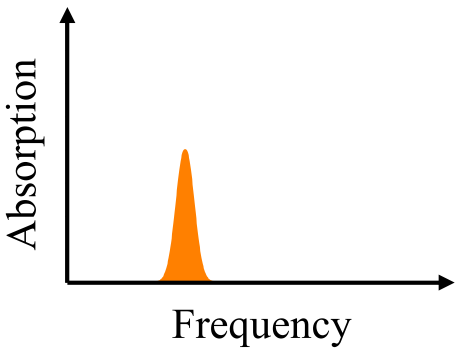




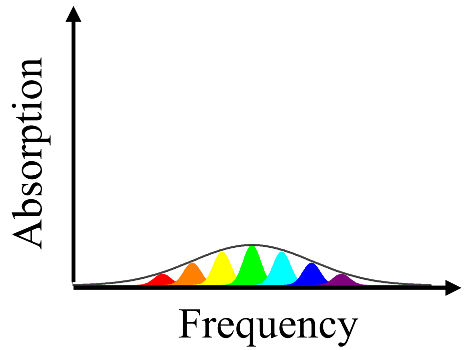
If the surroundings of the dye molecule are in a liquid state, the HB spectrum does not depends on excitation frequency.

HB spectrum





HB spectra at two excitation frequencies
Returns to the absorption spectrum

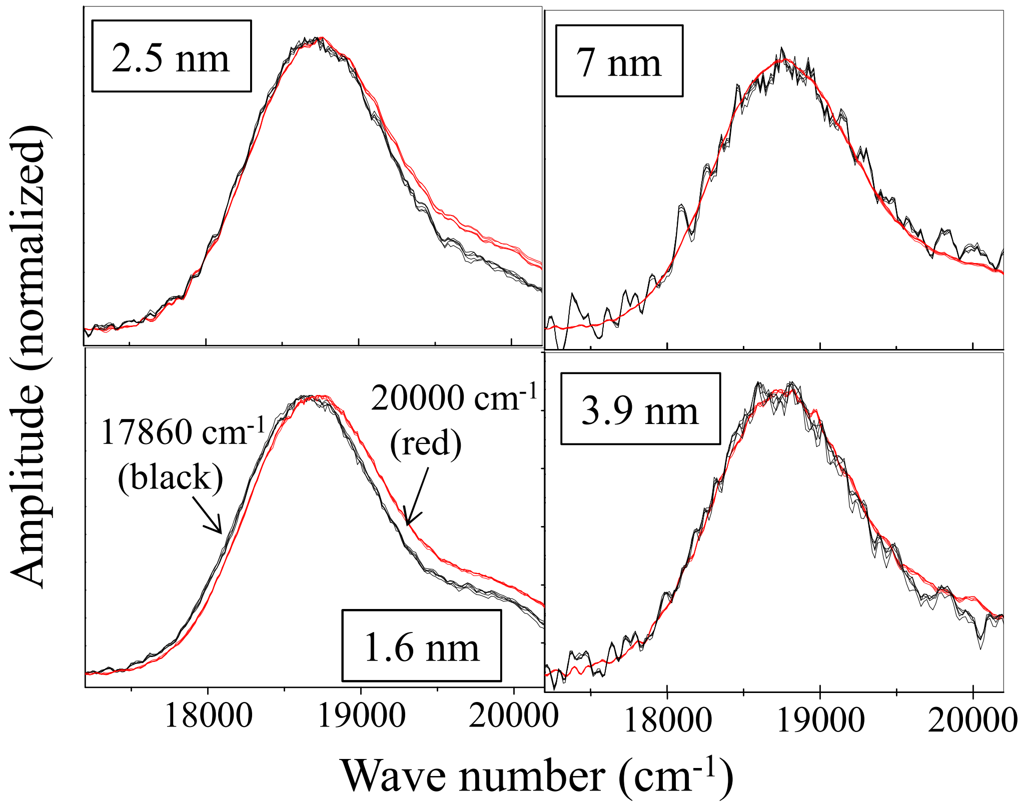


Configurational relaxation
to the thermal equilibrium

What we did in the present study:

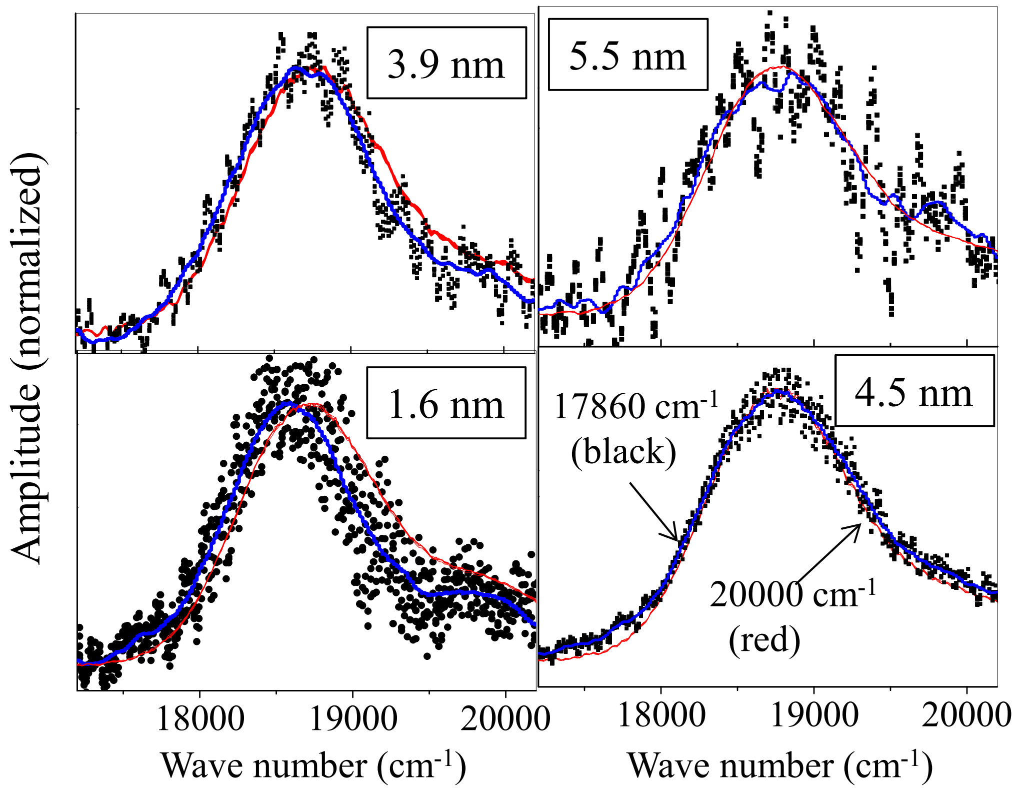
1. To measure HB spectra at two excitation frequencies (20000 cm^{-1} and 17860 cm^{-1})
2. To make comparison between them in the aqueous-cavity diameter from $\sim$1.6 nm to $\sim$7 nm
3. To determine whether the surrounding water of the dye molecule is in a glassy or liquid state at each size

Change from a liquid to a glassy state with decreasing the size

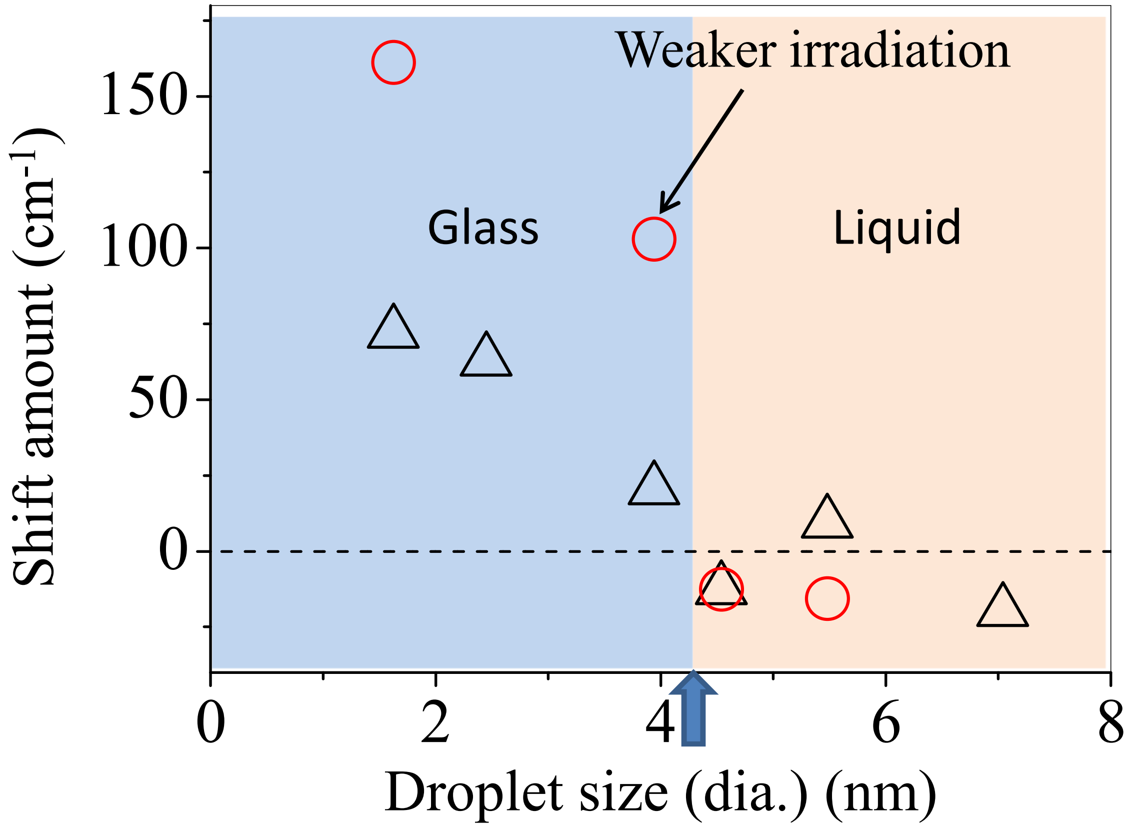


- The two spectra agree at 7 nm. → Liquid state
- The difference between them becomes clear with decreasing the size.
- Clear spectral shift between the two spectra at 1.6 nm → glassy state
- There is the possibility that the saturation effect makes the site-selectivity obscure.

Case of HB spectra at 17860 cm^{-1} under weaker irradiation conditions



A spectral shift between the two spectra exists at 3.9 nm, whereas the two spectra agree above 4.5 nm.



Shift amount: difference between the midpoints of the spectra at the two excitation frequencies

Liquid-glass transition at ~ 4 nm
(~1600 water molecules in the reverse micelle)