Reorientation and Vibrational Energy Relaxation of Pseudo-halide Ions Confined in Reverse Micelle Water Pools

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BACKGROUND

Reverse Micelle Systems

- What are reverse micelles (RMs)?

  Nano-size water droplets solubilized in oil phase by surfactants.
  Water content = [water]/[surfactant]

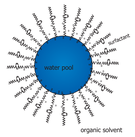
  Surfactants used:
  - anionic AOT - sodium bis(2-ethylhexyl) sulfosuccinate
  - cationic CTAB - cetyltrimethylammonium bromide
  - nonionic NP - nonylphenyl poly-oxyethylene

- Properties of RM water pool:

  Size and shape:
  - monodisperse for small
  - nanometer spheres, radius increases with
    - AOT RM: R(Å) ~ 2 in n-heptane
    - NP RM: R(Å) ~ 3 in cyclohexane

  Static properties:
  - disrupted 3D H-bond network
  - reduced polarity/dielectric constant
  - different types of water
    - trapped: in between surfactants, isolated H_2O
    - bound: bonds directly/indirectly to interface
    - free: resemble but not equivalent to bulk water

  Dynamical properties:
  - rate suppression in RMs: low translational/rotational mobility



Time-resolved IR Spectroscopy in Liquid

- Vibrational energy relaxation (VER):
  - VER pathways:
    - Internal - IVR (solvent assisted)
    - External - to solvent
  - VER time (T_1) depends on :
    - vibrational frequency
    - anharmonicity
    - solute-solvent interaction

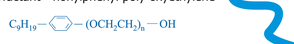
- Early results on anions in bulk:

	solvent	T_1(ps)	T_R(ps)	(cm^{-1})
N_3	MeOH	2.4	12.7	56
OCN	MeOH	2.9	6.7	37
SCN	MeOH	18.3	4.7	0
CN	H_2O	25	1	

- Ultrafast VER rate due to strong Coulomb interaction
- Inverse relations between VER rate and reorientation time (T_R)
- : bulk solvent shift from gas phase

NP RMs Recipe:

surfactant - nonylphenyl poly-oxyethylene

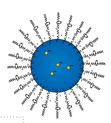


NP7: n=7; NP4: n=4
V_{NP7}/V_{NP4} = 4

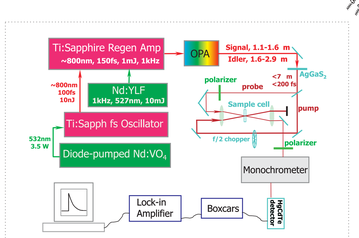
IR band of pseudohalide ions as a probe:

advantages:
- large solubility in water
- small size
- strong IR band around 2000 cm^{-1}
- big solvent shift in H_2O

FTIR and Ultrafast IR Spectroscopy of Pseudohalide Ions in RMs



Ultrafast Experimental Setup



- Two-color pump-probe

  broad band pump: center @ = 1 ← 0 transition
  frequency-resolved probe @ = 2 ← 1 transition

- Polarization resolved

  : polarization angle between pump and probe
  r : anisotropy

Population decay:

= 54.7°

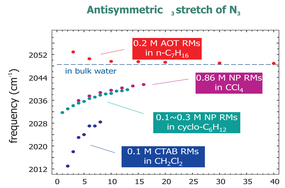
$$I(t) \quad I_0 e^{\ t/T_1}$$

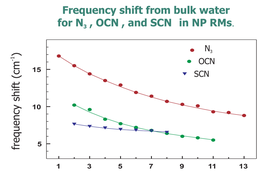
Anisotropy decay:

$$r(t) \quad \frac{I_{//} \quad I}{I_{//} \quad 2I} \quad 0.4e^{\ t/T_R}$$

I = 0°; $I_{,}$ = 90°

FTIR Spectroscopy of Anions in Reverse Micelles



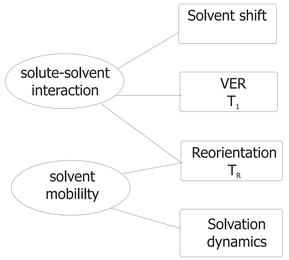


- The $_3$ frequency of N_3 ion:
  - AOT RMs: blue shift
  - NP and CTAB RMs: red shift
  - all RMs: the shift decreases with increasing
  - no dependence on:
    - azide ion concentration
    - surfactant concentration
  - blue shift with [alkali$^+$] in bulk
  - OCN similar to N_3 smaller shift in SCN vs.

- Frequency shift may depend on:
  - charge of the surfactant
  - location of the ions
  - polarity of water in RMs
  - presence of counter ions (AOT)

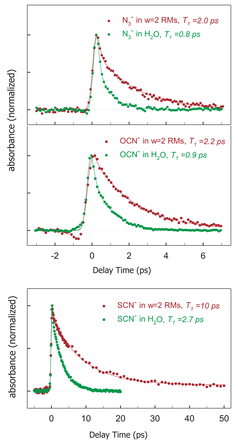
Frequency shift in NP RMs relative to bulk water ( ), vibrational energy relaxation time (T_1) and reorientation time (T_R) of N_3 , OCN , and SCN ions in 0.28 M NP reverse micelles in cyclohexane and in bulk H_2O.

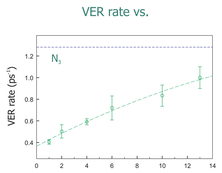
		=1	=2	=6	=10	bulk H_2O
	N_3	-16.8	-15.5	-11.9	-10.1	0
(cm^{-1})	OCN		-10.2	-7.2	-5.8	0
	SCN		-7.7	-6.9		0
T_1	N_3	2.5(0.2)	2.0(0.2)	1.4(0.2)	1.2(0.1)	0.8(0.1)
(ps)	OCN		2.2(0.2)	1.5(0.2)	1.2(0.1)	0.9(0.1)
	SCN		10(2)	6.4(1)		2.7(0.3)
T_R	N_3	>25		7.6(2)	5.5(1.5)	1.3(0.3)
(ps)	SCN		>100	>20		3.6(1)

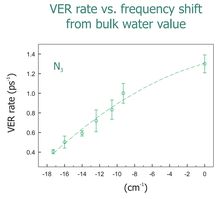


SCN different from OCN + N_3 ions:
- normal coordinate: localized in SCN
- charge distribution
- location of the ions
  SCN soluble in organic solvent
  prefer interface?

Vibrational Energy Relaxation in NP RMs



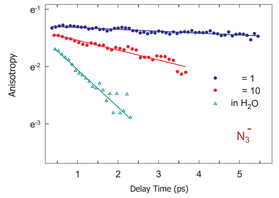


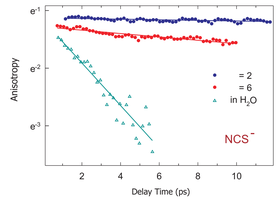


Transient absorption decay:
- two decay components:
  - instrument limited:
    due to Optical Kerr Effect (OKE)
  - single exponential dynamics: VER

Vibrational Energy Relaxation:
- rate suppression in small RMs
- T_1 decreases with increasing
- concentration independent (1-4 M)
- N_3 and OCN similar at all
  SCN slower in both RMs and in H_2O

Orientational Relaxation in NP RMs





Anisotropy decay:
- no data at t<0.5 ps due to OKE
- single exponential fit:
  fast T_1 → short observation window
  only lower limit for T_R in small RMs.
- little reorientation in small
- T_R decreases with increasing
- T_R decreases with [N_3] possible intermolecular resonant energy transfer

SUMMARY

Static and time-resolved IR spectroscopy studies of N_3 , OCN , and SCN ions in RMs:

- Results in RMs different from in bulk water:
  - Smaller solvent shift
    surfactant dependent
  - Longer VER and reorientation times
  - Approach bulk value with increasing

- Slower dynamics in RMs
  - Opposite correlation between T_1 and T_R than in bulk
  - VER rate reduction
    - * Less dramatic than solvation dynamics
    - * Consistent with low polarity of water in RMs
    - * RMs provide a way to vary friction amplitude for dynamical studies of ions in solution
  - Reorientation slower
    - * Comparable to solvation dynamics
    - * Consistent with restricted mobility of water in RMs

- Water droplet in RMs become more bulk-like at large

  solvent shift, VER rate, and reorientation time approach bulk value

- Vibrational spectroscopy of inorganic ions as a novel probe for RM systems

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