New Insights into Cation- and Temperature-Driven Protein Adsorption to the Air−Water Interface through Infrared Reflection Studies of Bovine Serum Albumin

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Present by Sam Sokhuoy

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New Insights into Cation- and Temperature-Driven Protein Adsorption to the Air–Water Interface through Infrared Reflection Studies of Bovine Serum Albumin

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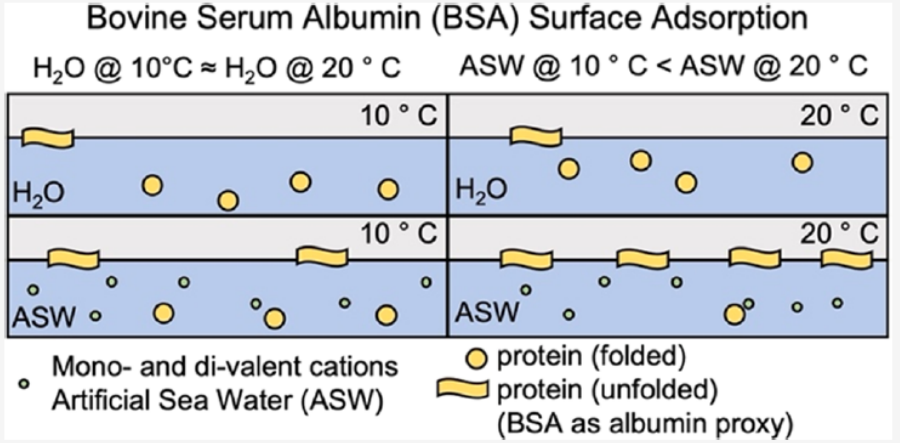
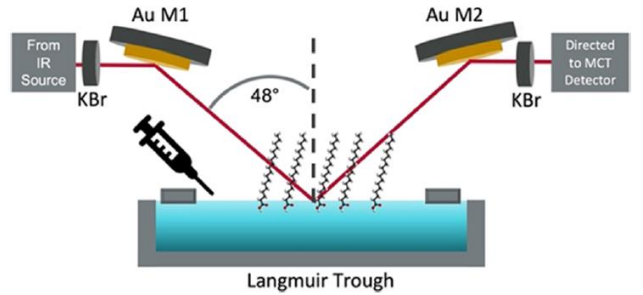
ABSTRACT: The chemistry and structure of the air–ocean interface modulate biogeochemical processes between the ocean and atmosphere and therefore impact sea spray aerosol properties, cloud and ice nucleation, and climate. Protein macromolecules are enriched in the sea surface microlayer and have complex adsorption properties due to the unique molecular balance of hydrophobicity and hydrophilicity. Additionally, interfacial adsorption properties of proteins are of interest as important inputs for ocean climate modeling. Bovine serum albumin is used here as a model protein to investigate the dynamic surface behavior of proteins under several variable conditions including solution ionic strength, temperature, and the presence of a stearic acid ($C_{17}COOH$) monolayer at the air–water interface. Key vibrational modes of bovine serum albumin are examined via infrared reflectance–absorbance spectroscopy, a specular reflection method that ratios out the solution phase and highlights the aqueous surface to determine, at a molecular level, the surface structural changes and factors affecting adsorption to the solution surface. Amide band reflection absorption intensities reveal the extent of protein adsorption under each set of conditions. Studies reveal the nuanced behavior of protein adsorption impacted by ocean-relevant sodium concentrations. Moreover, protein adsorption is most strongly affected by the synergistic effects of divalent cations and increased temperature.



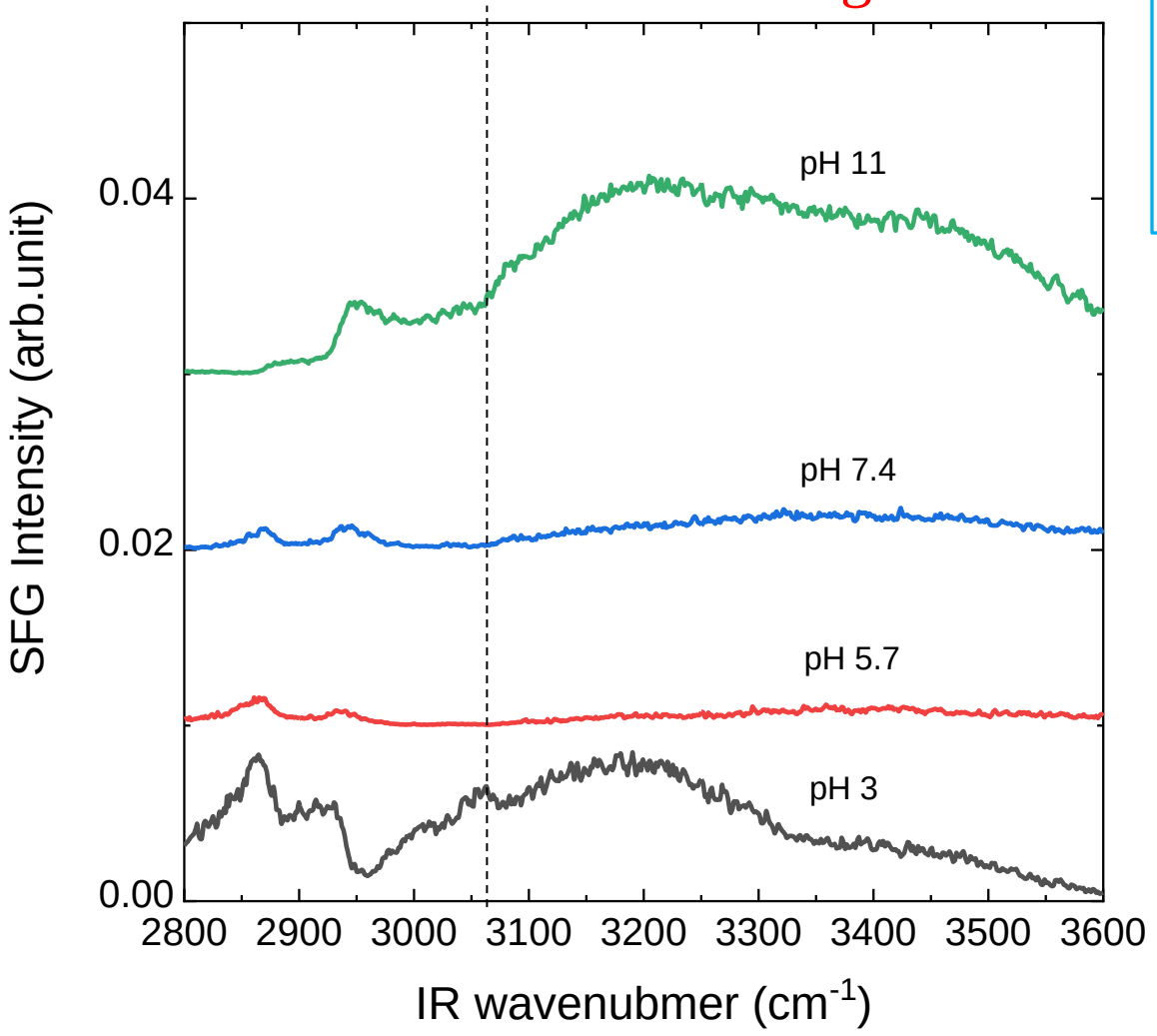
❑ Main Idea

- ❑ Sea salts and temperature affect dynamics and adsorption at the surface behavior of BSA using IRRAS



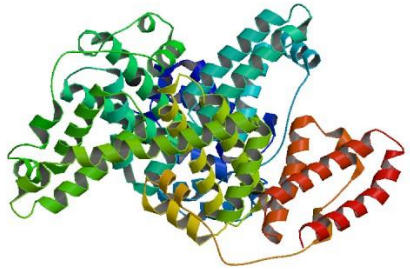
❑BSA at different pH

❑CH of aromatic ring



❑ Bovine serum albumin(BSA)

IEPS: BSA (pH ~ 5.5)



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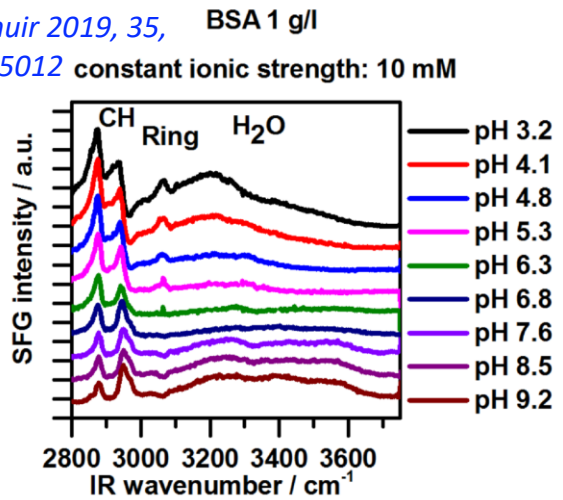

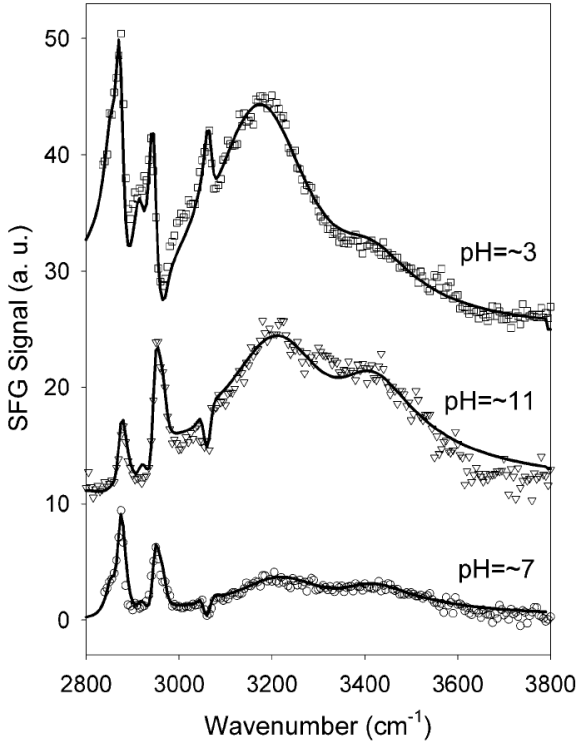

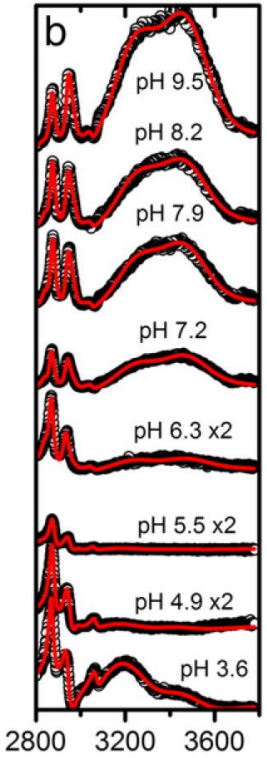

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Salting Up of Proteins at the Air/Water Interface

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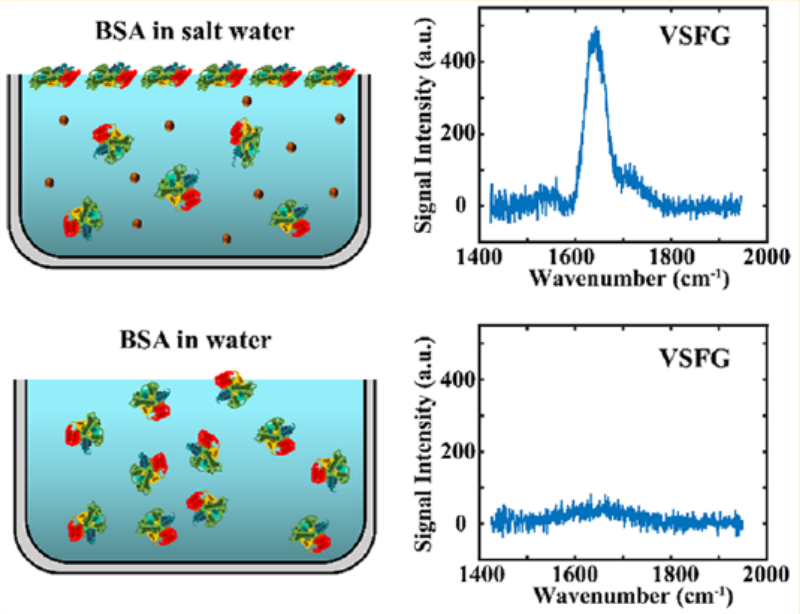
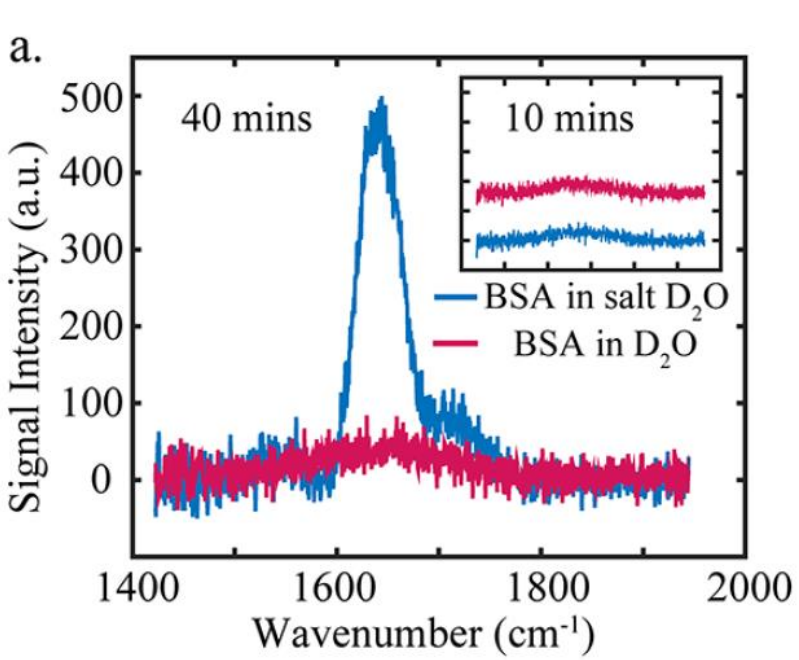
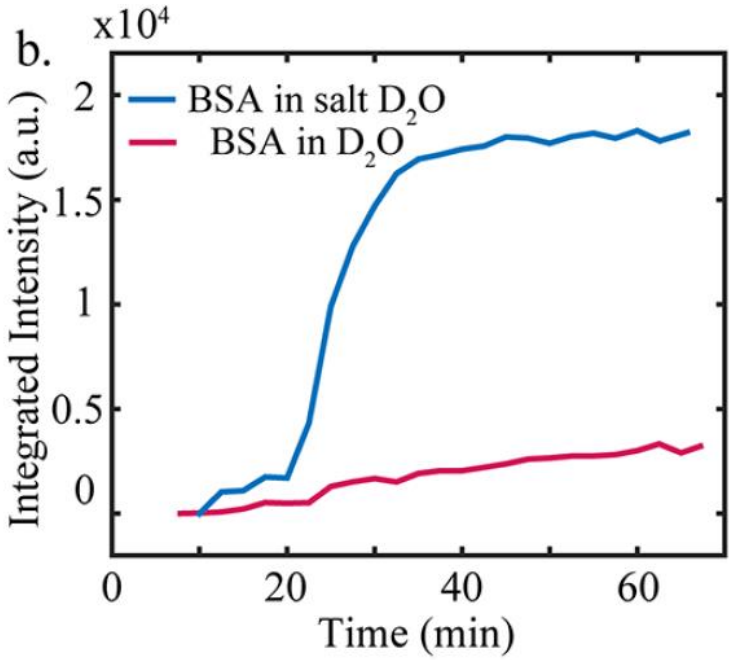
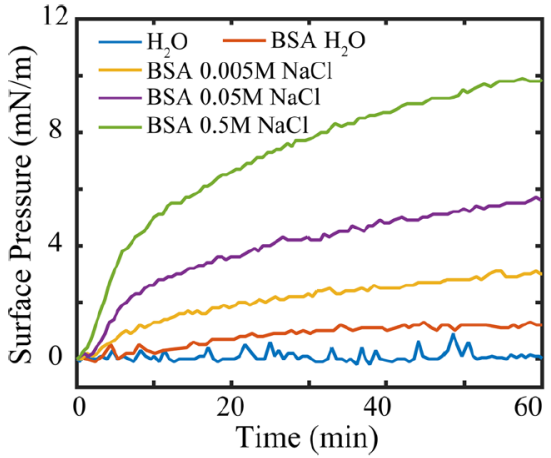
Supporting Information

ABSTRACT: Vibrational sum frequency generation (VSFG) spectroscopy and surface pressure measurements are used to investigate the adsorption of a globular protein, bovine serum albumin (BSA), at the air/water interface with and without the presence of salts. We find at low (2 to 5 ppm) protein concentrations, which is relevant to environmental conditions, both VSFG and surface pressure measurements of BSA behave drastically different from at higher concentrations. Instead of emerging to the surface immediately, as observed at 1000 ppm, protein adsorption kinetics is on the order of tens of minutes at lower concentrations. Most importantly, salts strongly enhance the presence of BSA at the interface. This "salting up" effect differs from the well-known "salting out" effect as it occurs at protein concentrations well-below where "salting out" occurs. The dependence on salt concentration suggests this effect relates to a large extent electrostatic interactions and volume exclusion. Additionally, results from other proteins and the pH dependence of the kinetics indicate that salting up depends on the flexibility of proteins. This initial report demonstrates "salting up" as a new type of salt-driven interfacial phenomenon, which is worthy of continued investigation given the importance of salts in biological and environmental aqueous systems.









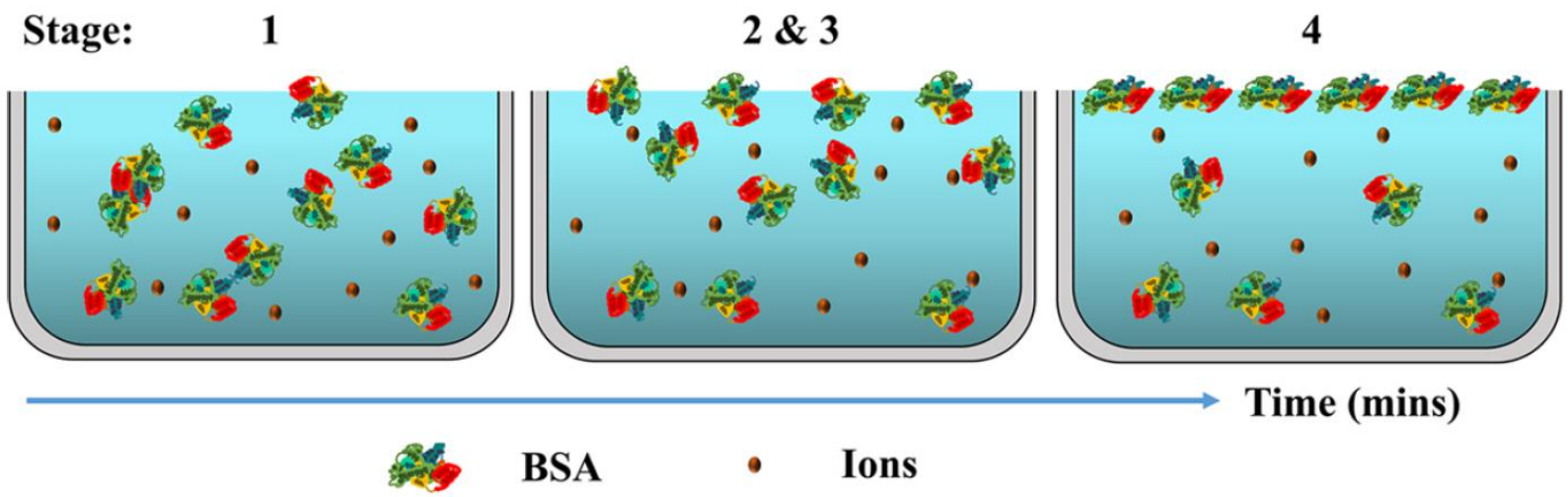


Figure 4. Surface pressure of 5 ppm BSA in different NaCl concentration solution.

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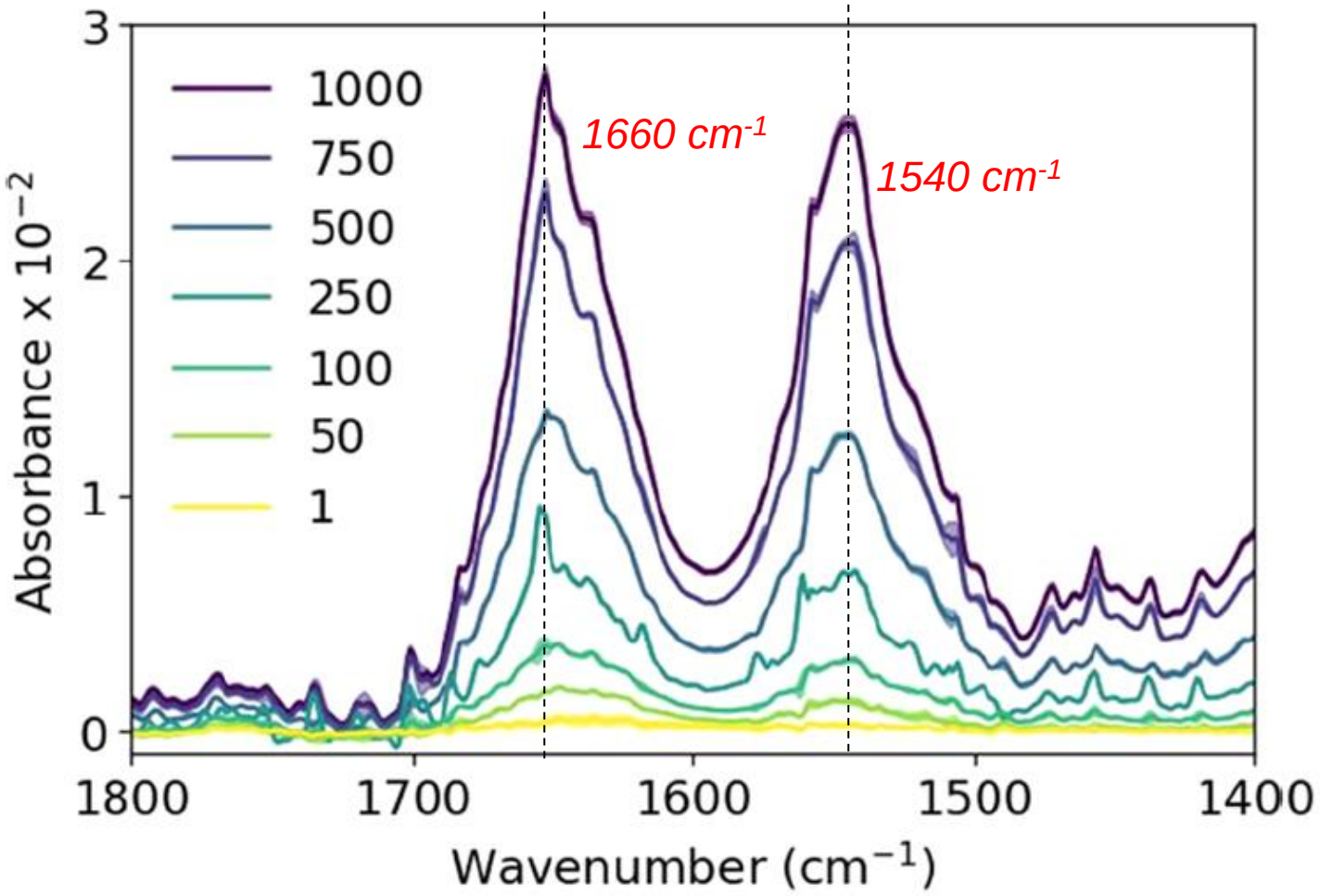
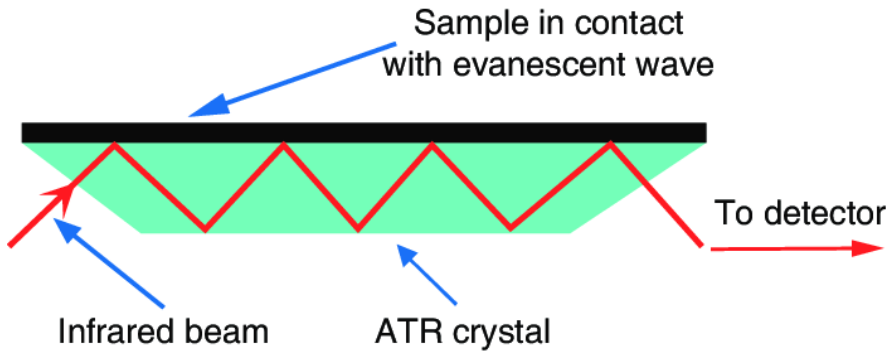
❑ ATR-FTIR results

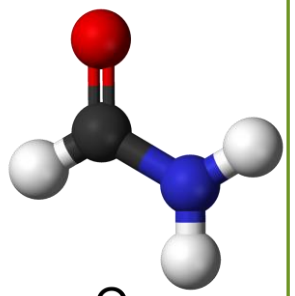
Water on ATR crystal is background and sample is BSA in water

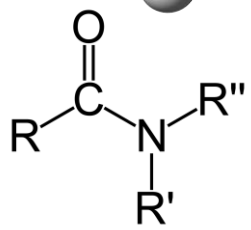
BSA at different concentration



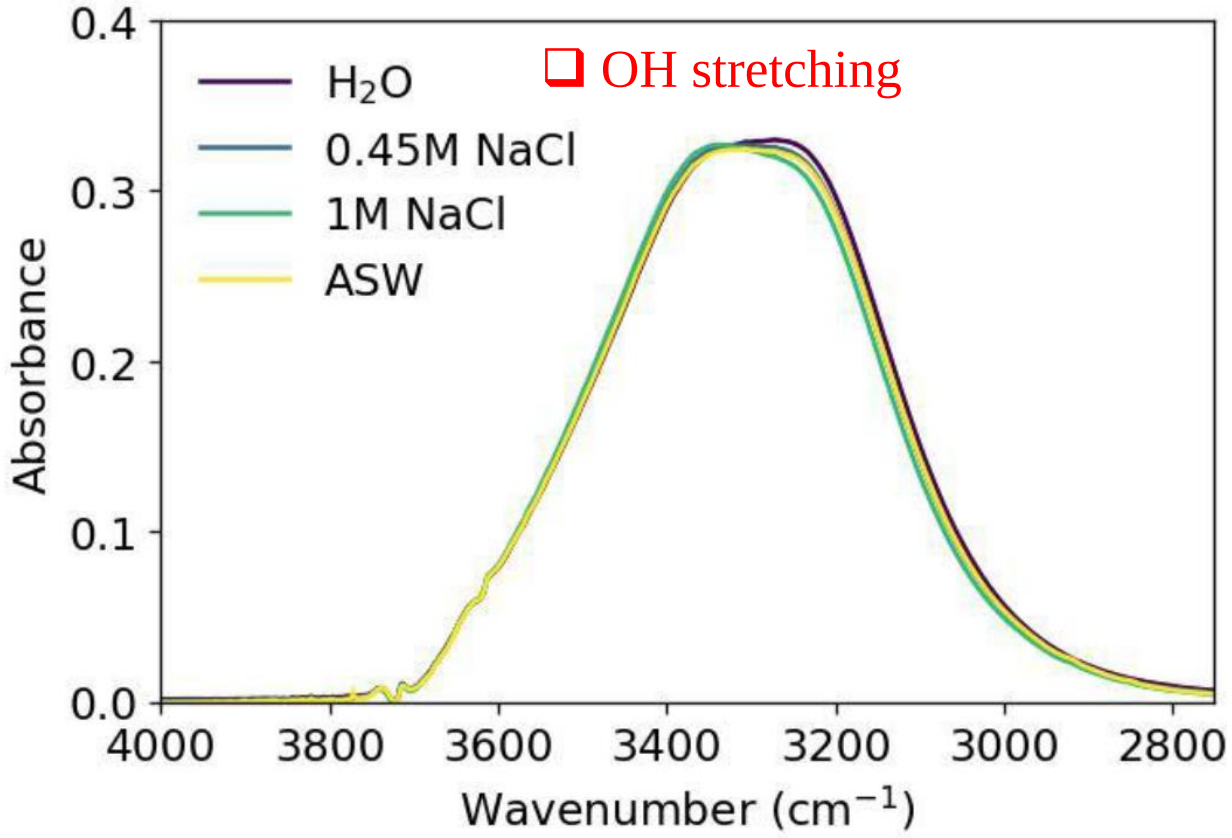


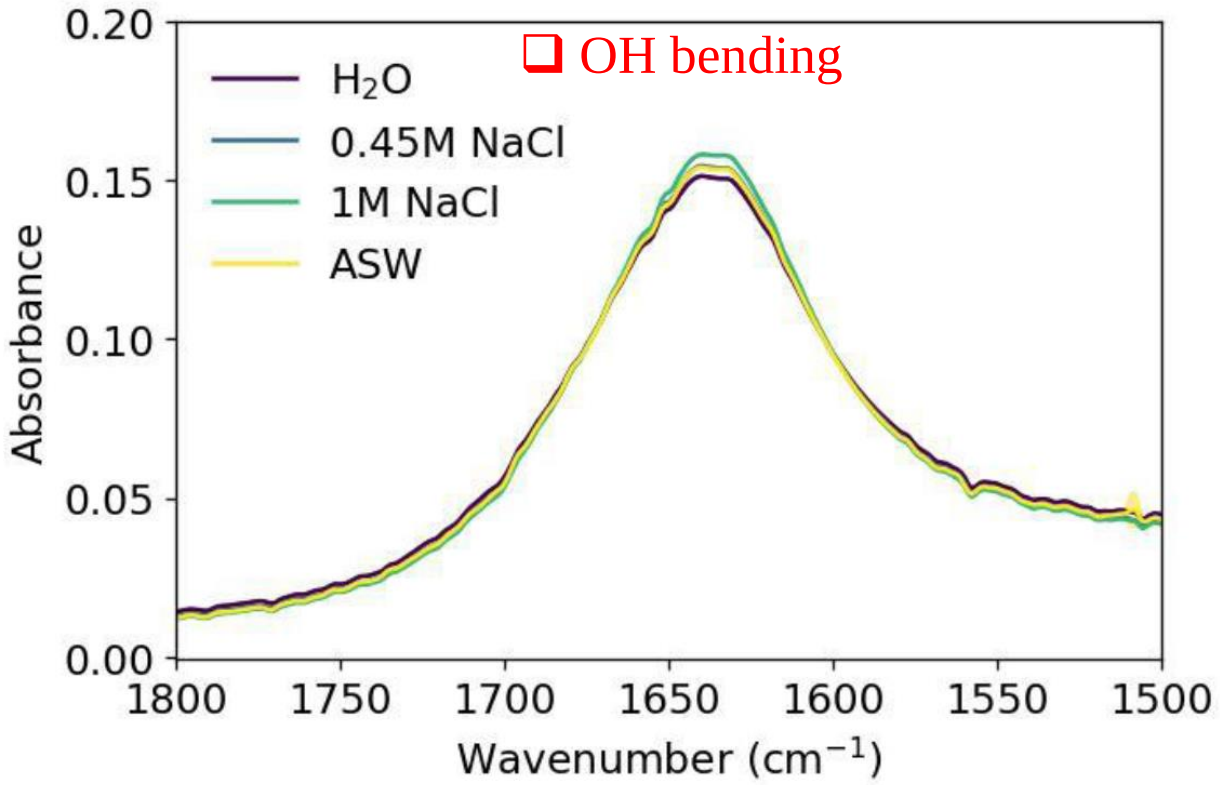
❑ Amide





❑No affected from the solution in OH and amide region





❑ Amide region from SFG

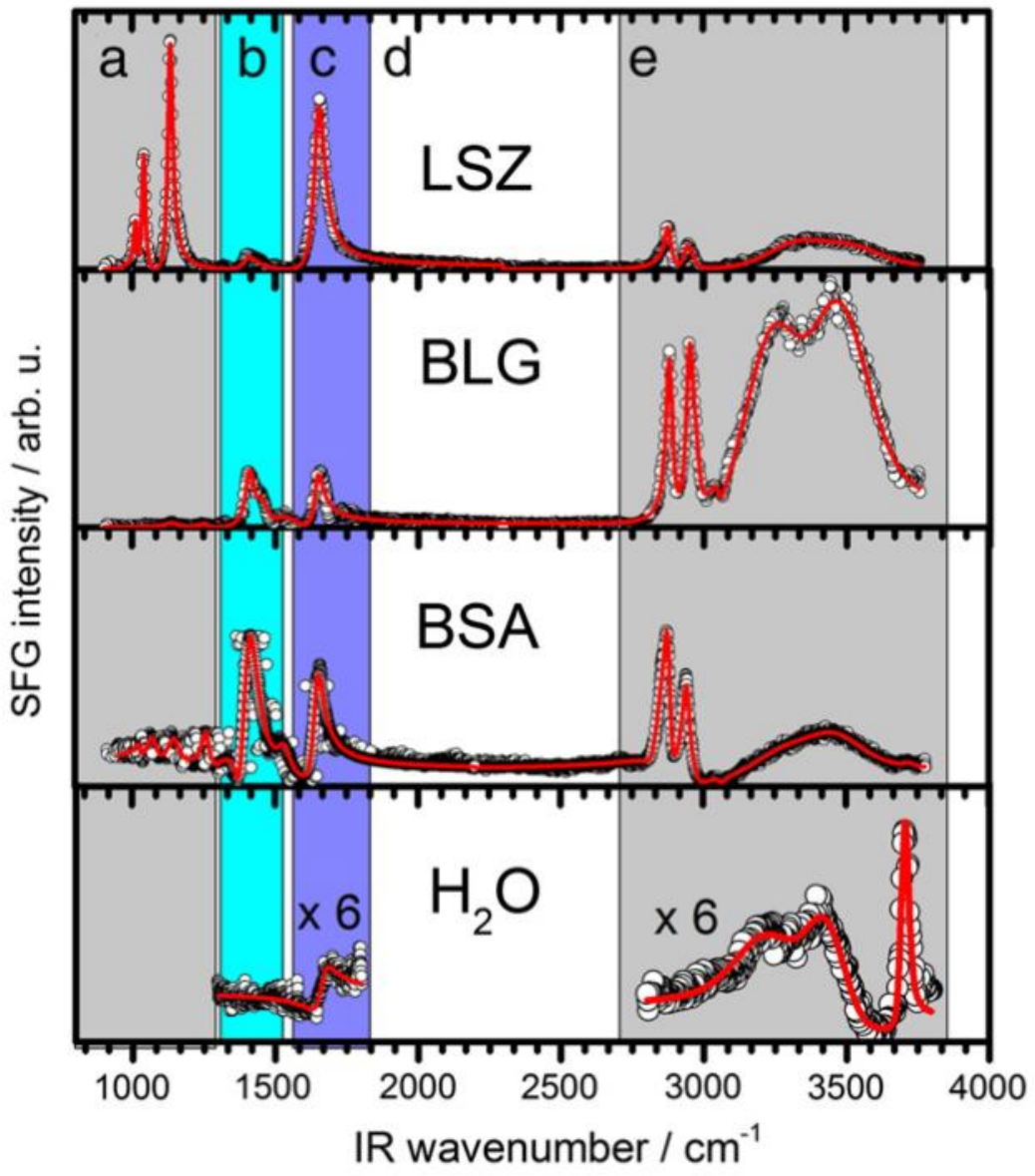


Table 1
Assignments of vibrational bands.

Band[a]	[cm^{-1}]	Ref.
Amide III	1250	[44,45]
COO^- (ss)	1410	[38]
Amide II	1550	[48]
Amide I	1650	[49,50]
H_2O bending	1660	[41]
CH_3 (ss)	2875	[46,43,47•]
CH_3 (F)	2936	[46,43,47•]
Arom. CH	3070	[46,43,47•]
OH (ss)	3200	See discussion
OH (ss)	3450	See discussion
Dangling OH	3700	[42,51,35]

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❑ Property of salts in instant ocean

A. Ion/element concentrations for Instant Ocean from manufacturer

Ion	Instant Ocean (ppm)
Cl^-	19,290
Na^+	10,780
SO_4^{2-}	2,660
Mg^{2+}	1,320
K^+	420
Ca^{2+}	400
CO_3^{2-} /HCO^{3-}	200
Br^-	56
$Sr2^+$	8.8
B	5.6
F^-	1.0
Li^+	0.3
I^-	0.24
Ba^{2+}	Less than 0.04
Fe	Less than 0.04
Mn	Less than 0.025
Cr	Less than 0.015
Cu	Less than 0.015
Ni	Less than 0.015
Se	Less than 0.015
V	Less than 0.015
Zn	Less than 0.015
Mo	Less than 0.01
Al	Less than 0.006
Pb	Less than 0.005
As	Less than 0.004
Cd	Less than 0.002
Nitrate	None
Phosphate	None

❑ Their system

Table 1. Three Different Ionic Strengths were Used to Evaluate the Adsorption of BSA to the Surface with and without a Competing Stearic Acid Monolayer at Both 10 and 20 °C; Experiments Outlined Here are for IRRAS Measurements

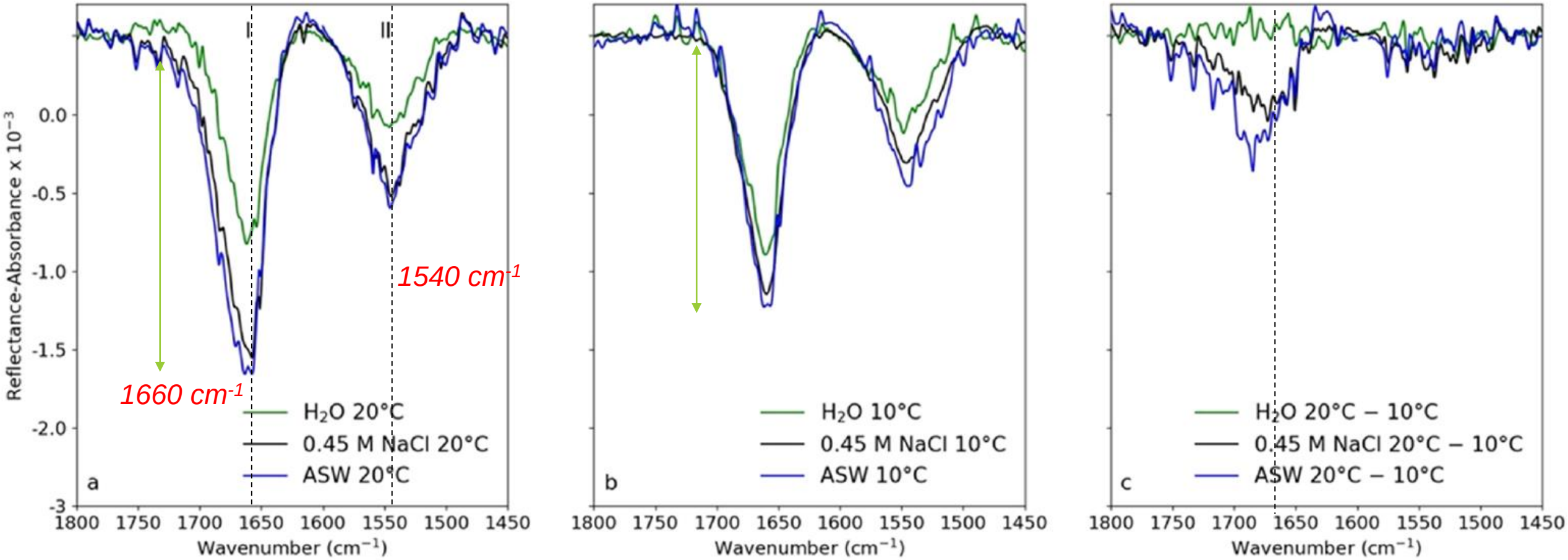
MilliQ H_2O				0.45 M NaCl				Instant Ocean			
no stearic acid		stearic acid		no stearic acid		stearic acid		no stearic acid		stearic acid	
10 °C	20 °C	10 °C	20 °C	10 °C	20 °C	10 °C	20 °C	10 °C	20 °C	10 °C	20 °C

❑ BSA-H_2O/0.45 M NaCl/ASW at 10 ^oC and 20 ^oC ❑ 0.37 μM BSA

❑ H_2O<NaCl<ASW

❑ The present of divalent cations (in ASW) is slightly increased compared to NaCl

20 ^oC *10 ^oC* *a-b*



❑ Concentration dependent of BSA in OH and amide region

C. Bovine serum albumin concentration dependent IRRAS

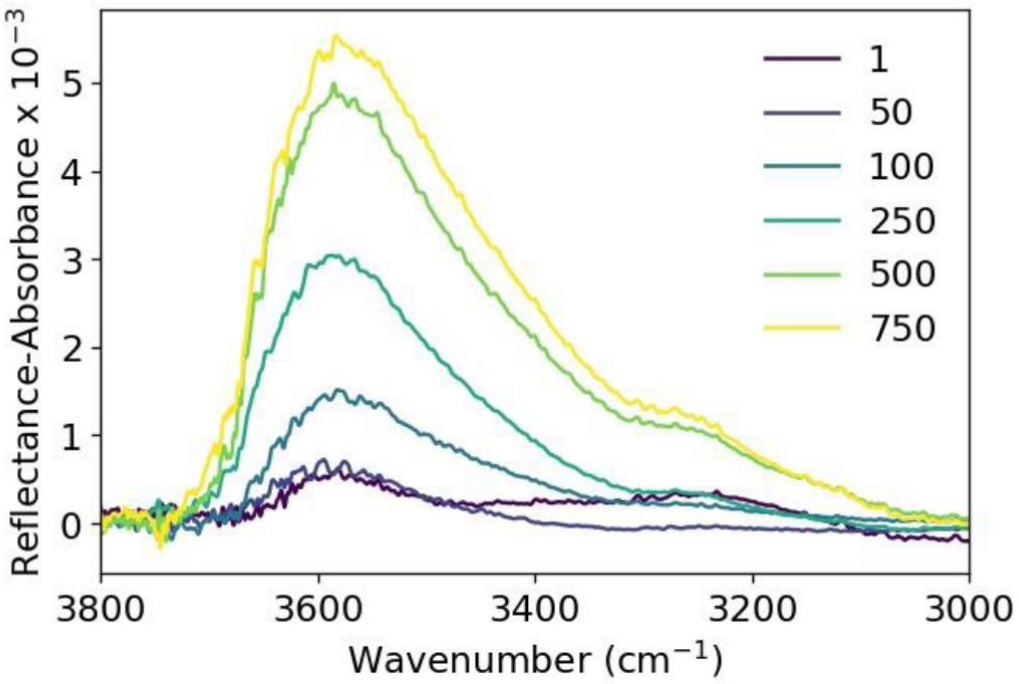


Figure S5. Background-corrected IRRAS showing O-H stretching region changes at variable BSA concentrations (given in μM). Injections of 1 and 50 μM solutions do not have a significant IR response as evidenced by the low intensity.

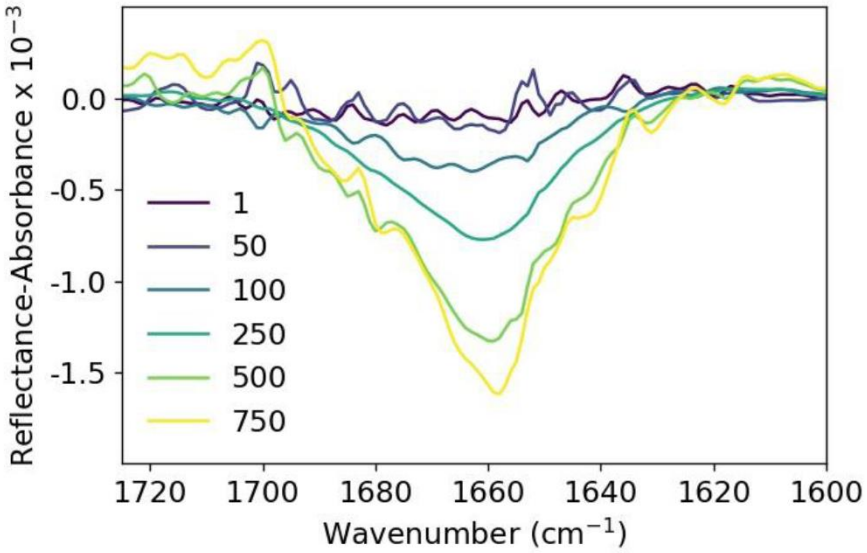
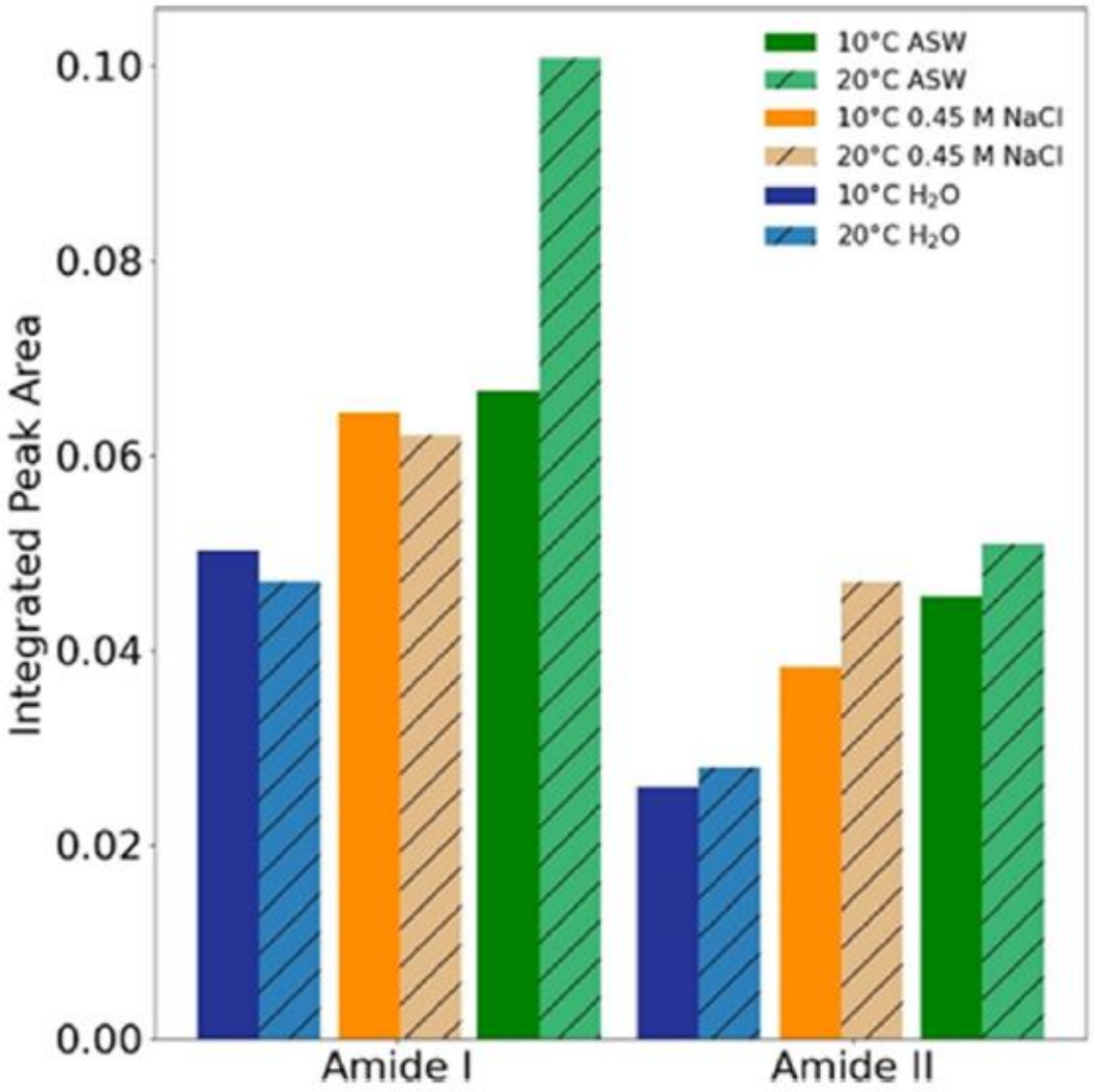


Figure S7. Background-corrected IRRAS showing amide I region changes at variable BSA concentrations (given in μM). Injections of 1 and 50 μM solutions do not have a significant IR response as evidenced by the low intensity.

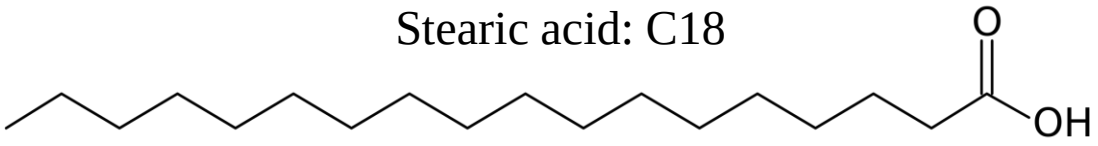
❑ Integrated peak area for Amide I&II



- At 20 ^{o}C ASW case provided the highest integrated area compared to other which represent the most absorption of BSA at the surface

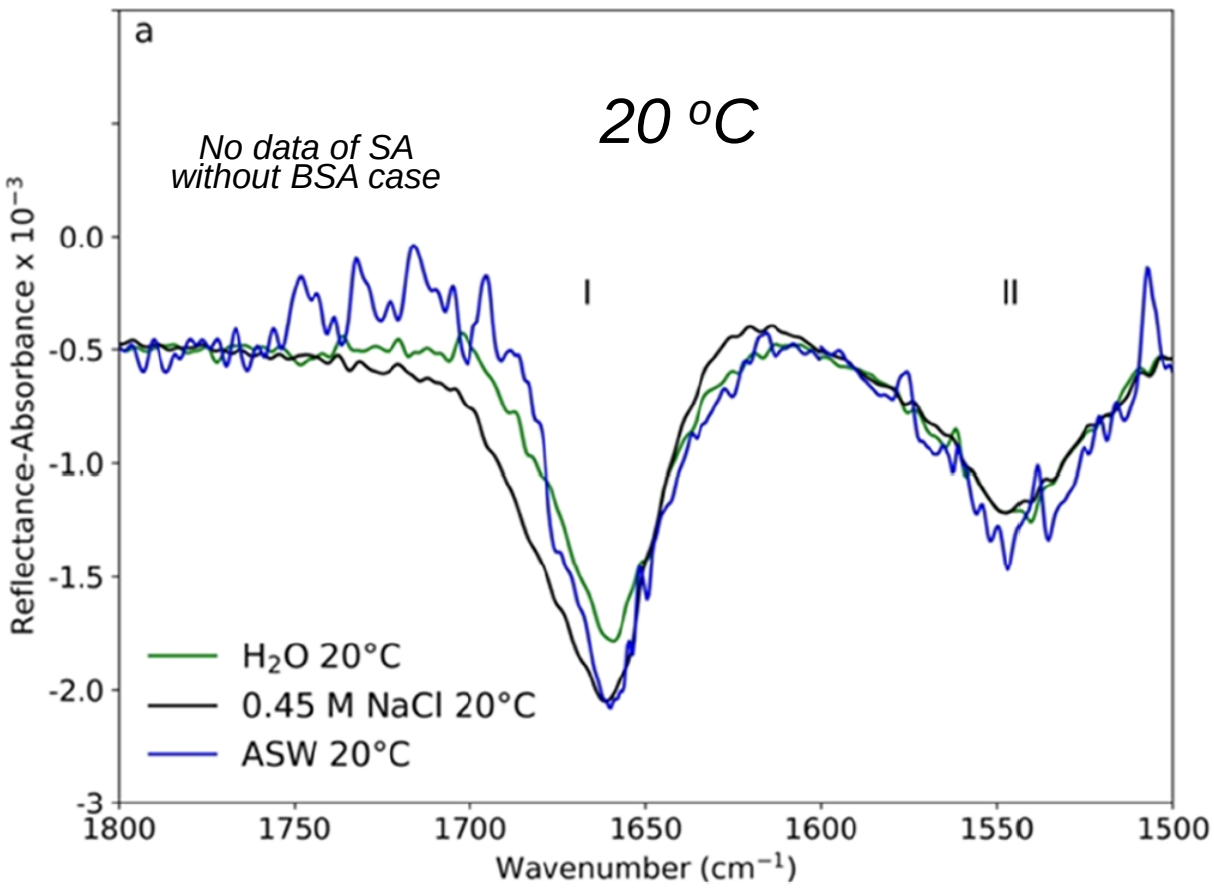
❑ SA (45 A^2/mol)-BSA at 10 ºC and 20 ºC (R_o is without BSA, R_M is after BSA injected)

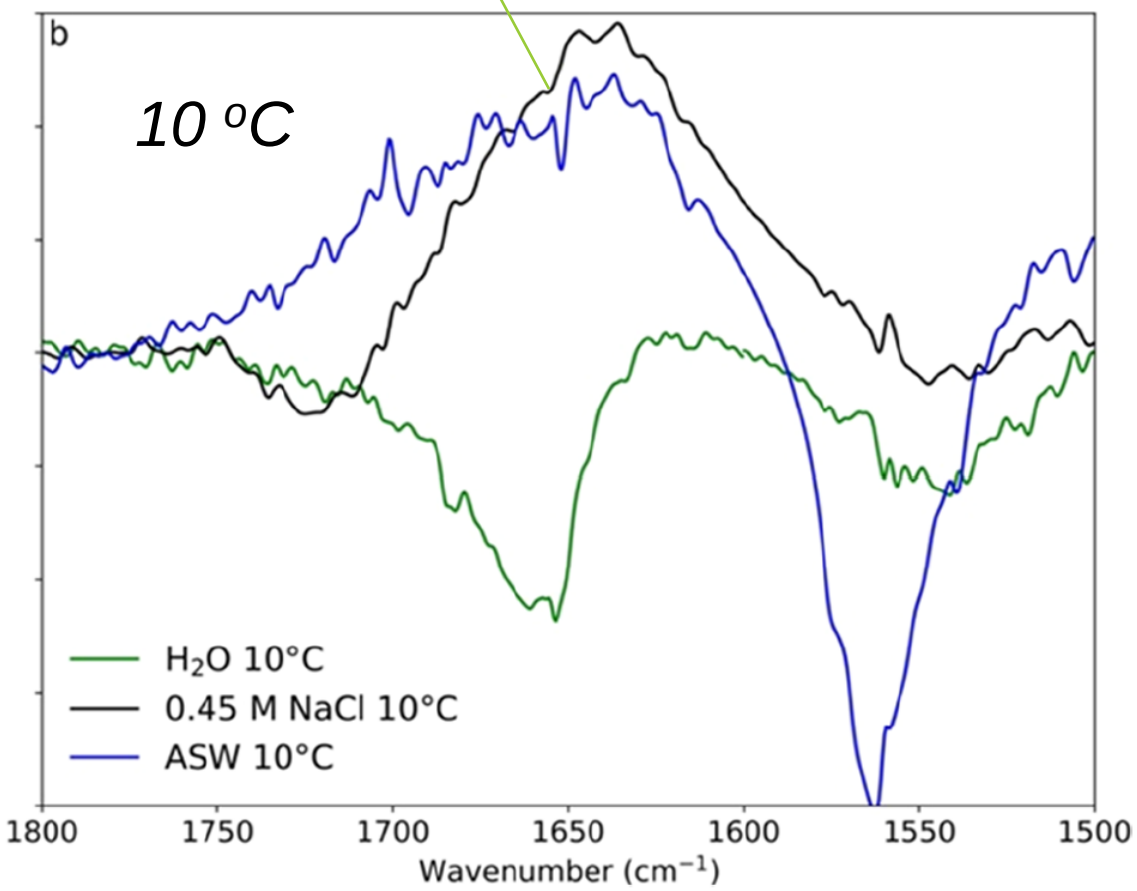
Stearic acid: C18



❑ Positive sign peak of amide I indicated that protein is below the surface

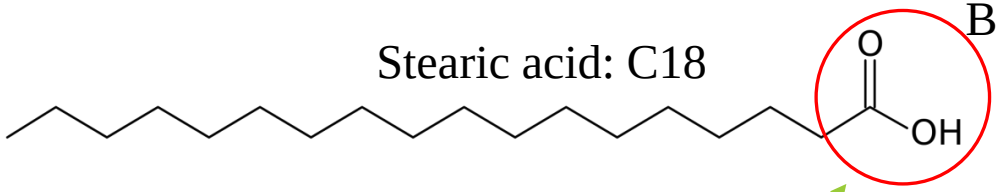
$$RA = -\log\left(\frac{R_M}{R_0}\right)$$

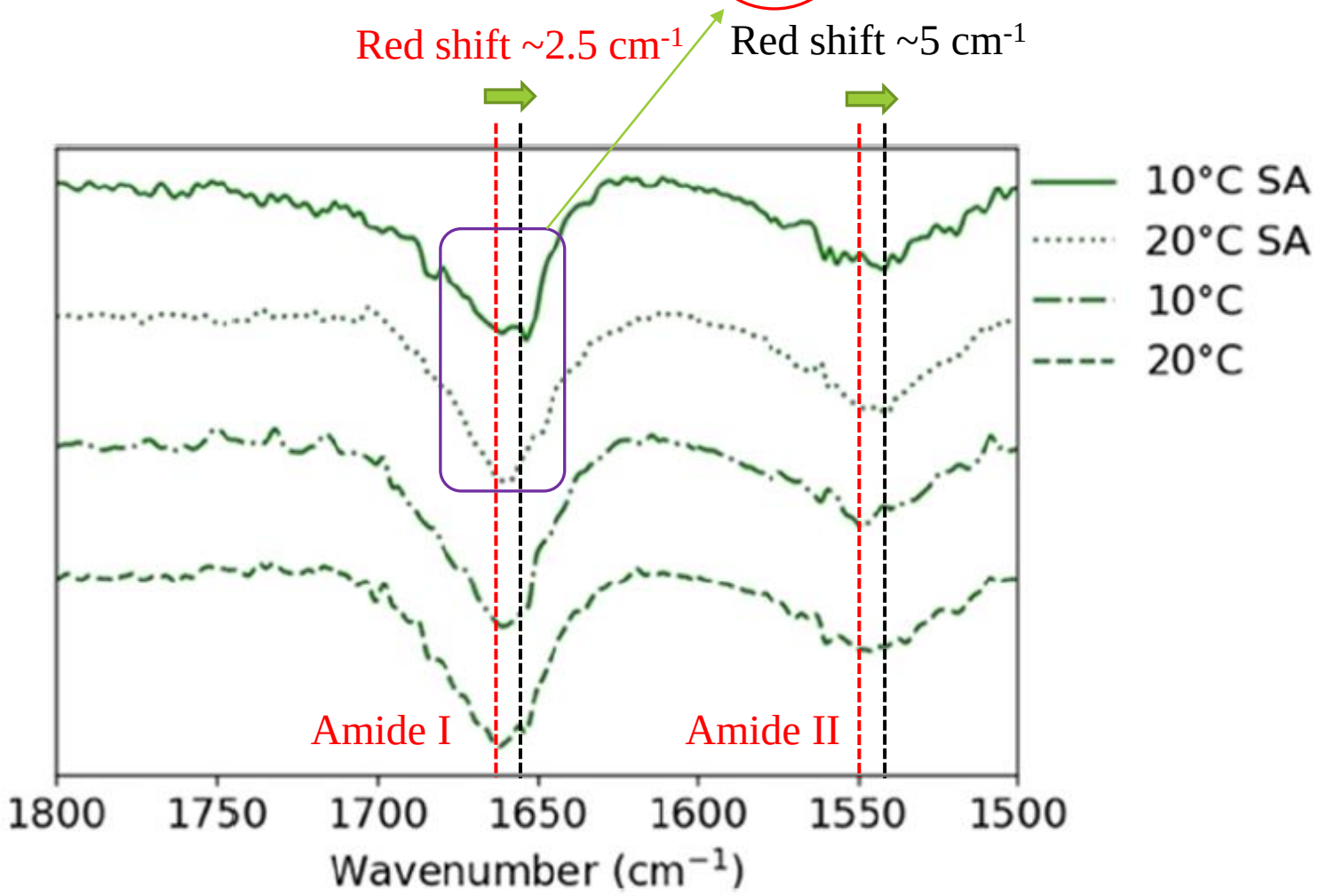




❑ SA-BSA at 10 °C and 20 °C

Convolution of amide from BSA and stearic acid headgroup





- ❑ The red shift represent the binding between BSA and SA through ion-dipole interaction such as, ionic bonds, bridging, and chelation.
- ❑ The blue shift of fatty acid headgroup represent the disorder of SA monolayer

❑ Summary

Salt and temperature affect the surface adsorption of BSA