Queens College
CITY UNIVERSITY OF NEW YORK

Formation, Characterization, and Application of Gas-Phase, Multiply Charged Reverse Micelles

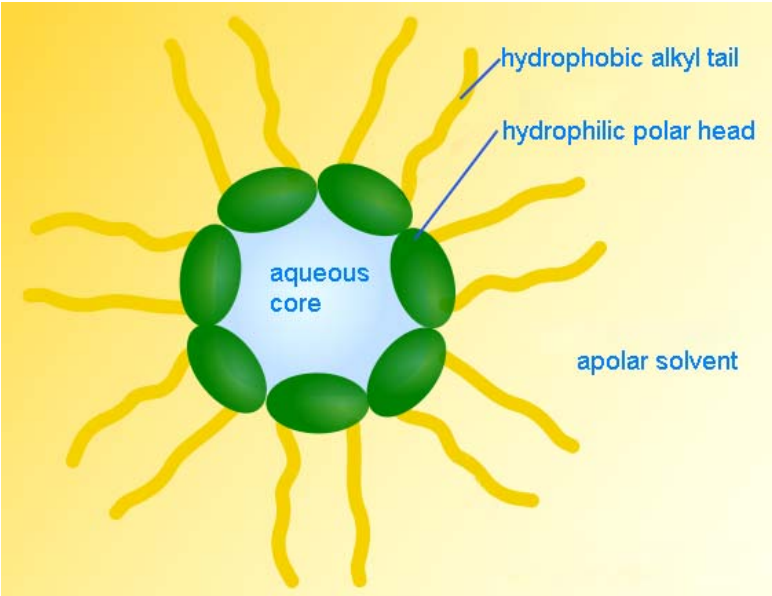
Jianbo Liu*, Yigang Fang, William Pineors

Department of Chemistry, Queens College &
The Graduate Center of the City University of New York

Spring 2010 ACS Meeting, San Francisco

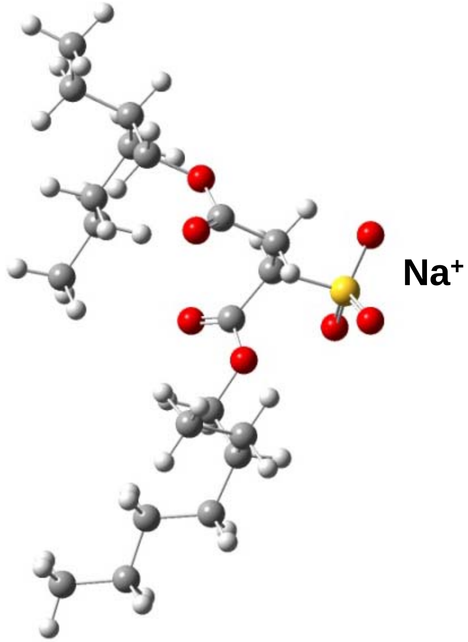
March 25, 2010

Reverse Micelles (RMs)



One of the most interesting nanometer-sized structures

- ❖ **selective encapsulation/solubilization**
- ❖ **catalysis**
- ❖ **membrane-mimetic system**



NaAOT, sodium bis(2-ethylhexyl) sulfosuccinate, a surfactant molecule commonly used for making RMs

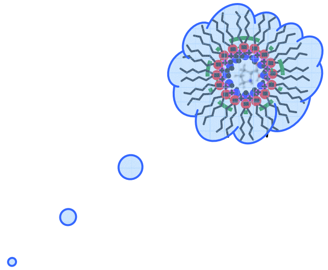
Formation of Gas-Phase RM

Approach

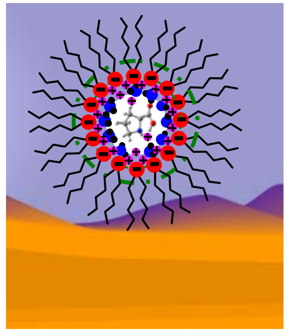
In Nature

(marine aerosols)

1. Formation of aerosol particles at the sea surface



2. Transfer of micelle-contained droplets to the gas phase, evaporation of water



3. RM in the gas-phase, maintaining encapsulated minerals and small organics

C. M. Dobson, G. B. Ellison, A. F. Tuck, V. Vaida. *PNAS*, **97**, 11864 (2000)

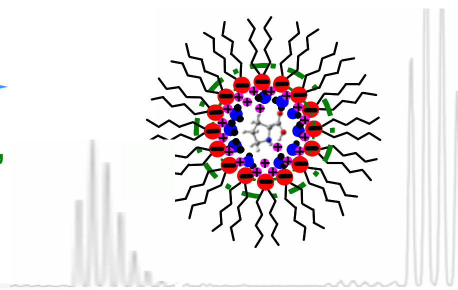
In Laboratory

Nano-electrospray ionization of micelle solution

Reverse micelle-contained droplets

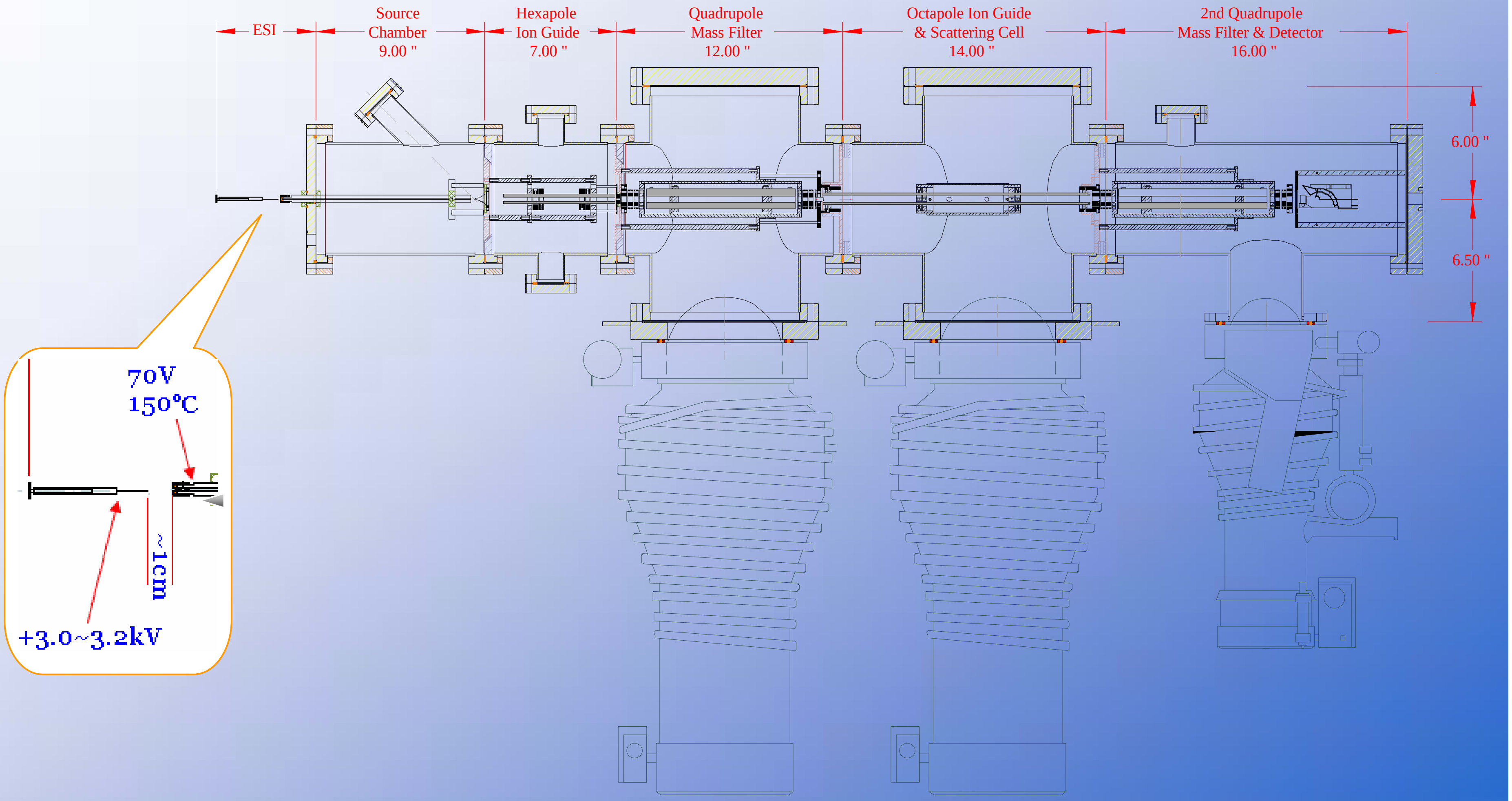
Transfer to the gas phase, removal of solvent, then exposure to the vacuum

RM in *vacuo*, encapsulating biomolecules



Y. Fang, A. Bennett, J. Liu, *Int J Mass Spectrom.* , in press (2010)

Instrument: ESI Guided-Ion-Beam Tandem Mass Spectrometer



Part I

Formation of Gas-Phase AOT RM & Encapsulation of Gly

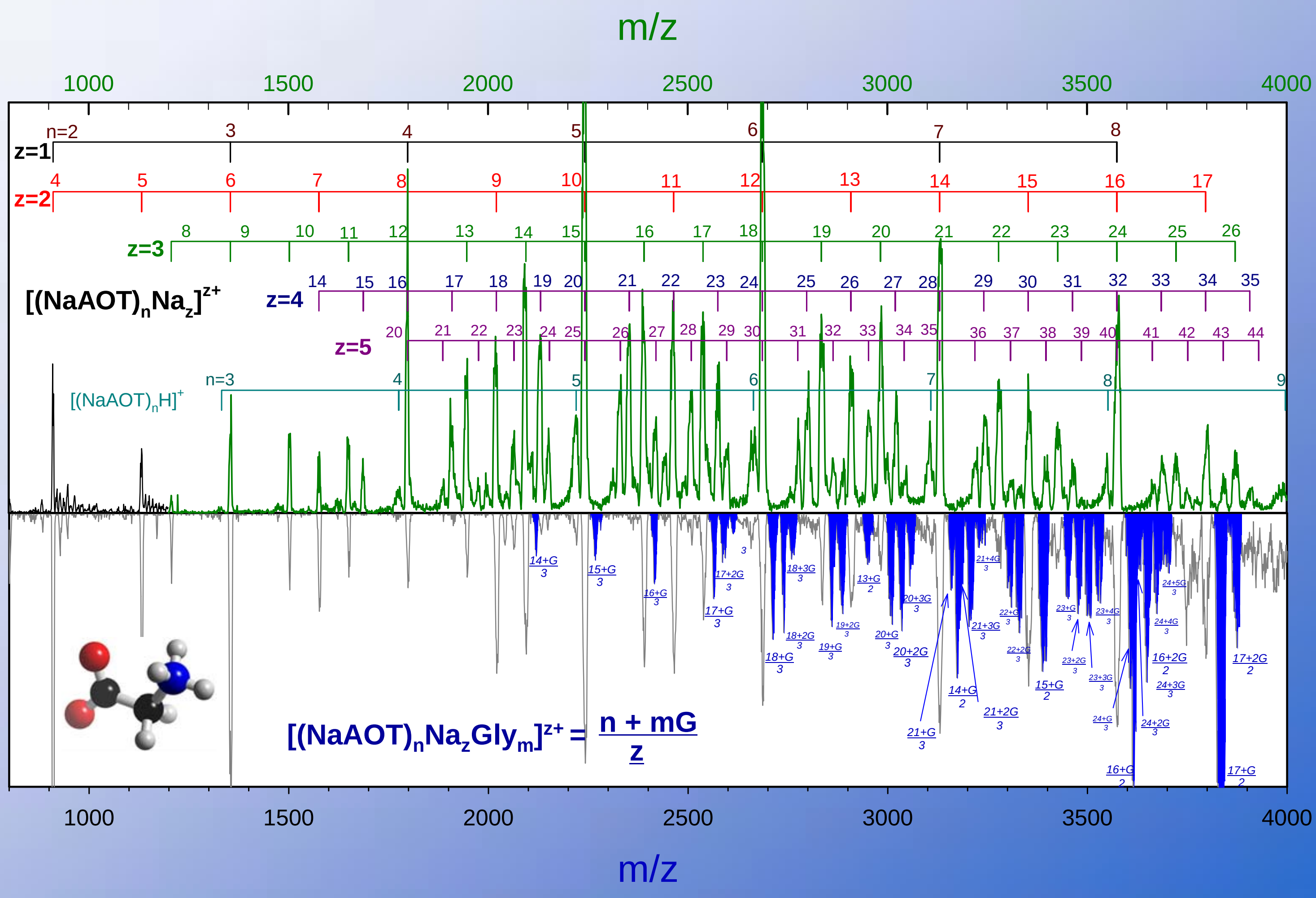
ESI solution:

5 mM NaAOT in hexane, ω_0 ([water]/[AOT]) = 10

[Similar spectrum was obtained using 5 mM NAOT in methanol/water]

ESI solution:

Same as above, except into which Gly was added ([Gly] = 1 mM)



Size Dependence of Gas-Phase RM Encapsulation

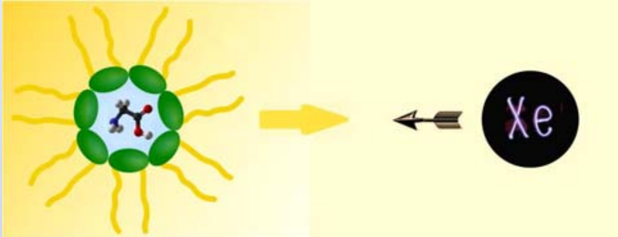
Aggregation number n	Core diameter (nm)	Max. number of Gly encapsulated in RM
$n < 13$	—	**0**
$n \geq 13$	**1.4**	**1**
$n \geq 16$	**1.6**	**2**
$n \geq 17$	**1.7**	**3**
$n \geq 21$	**1.9**	**4**
$n \geq 24$	**2.1**	**5**

Core diameter: $D = \sqrt{n \times A / \pi}$

A is the area of the AOT polar head (0.52 nm^2)

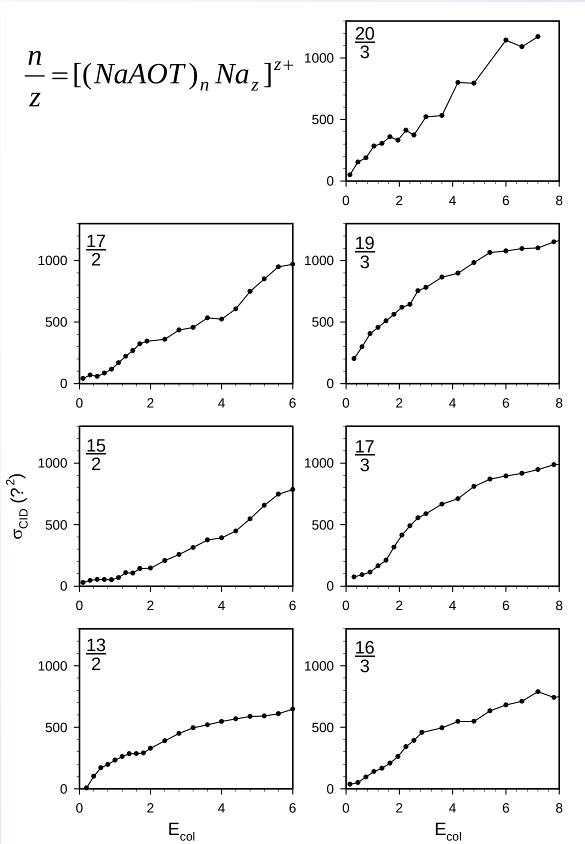
Size of Gly: 0.6-0.7 nm

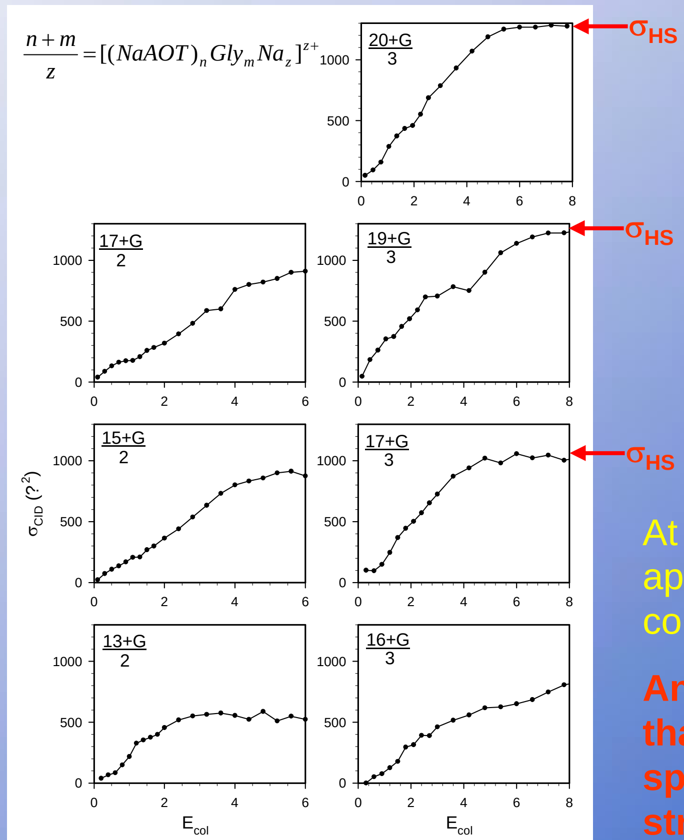
Collision-Induced Dissociation (CID) Cross Section As a Function of E_{col}

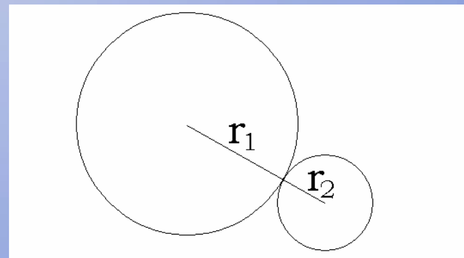


Empty gas-phase RM

Gas-phase RM encapsulating Gly







$$\sigma_{HS} = \pi \cdot (r_1 + r_2)^2$$

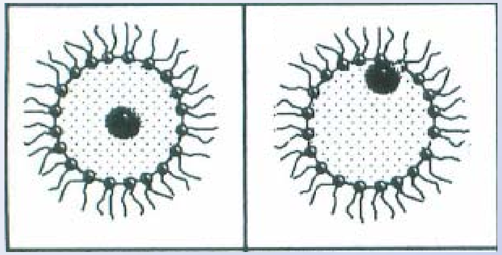
At highest E_{col}, σ_{cid} is approaching the hard-sphere collision limit →

Another piece of evidence that gas-phase AOT forms spherical reverse micellar structure

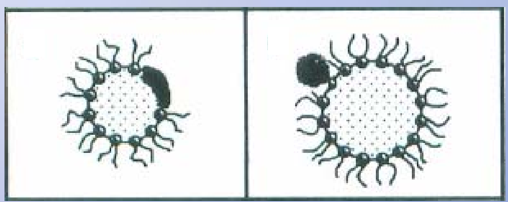
Part II Driving Forces for Solubilization:
Electrostatic vs. Hydrophobic

In Solution-Phase RM

Hydrophilic biomolecule (e.g. Gly, $TrpH^+$) located in the internal core
— electrostatic interaction



Hydrophobic biomolecule (e.g. neutral Trp) located at the interface
— hydrophobic interaction



P. L. Luisi, M. Giomini, M. P. Pileni, B. H. Robinson, *Biochimica et Biophysica Acta*, **947,** 209(1988)

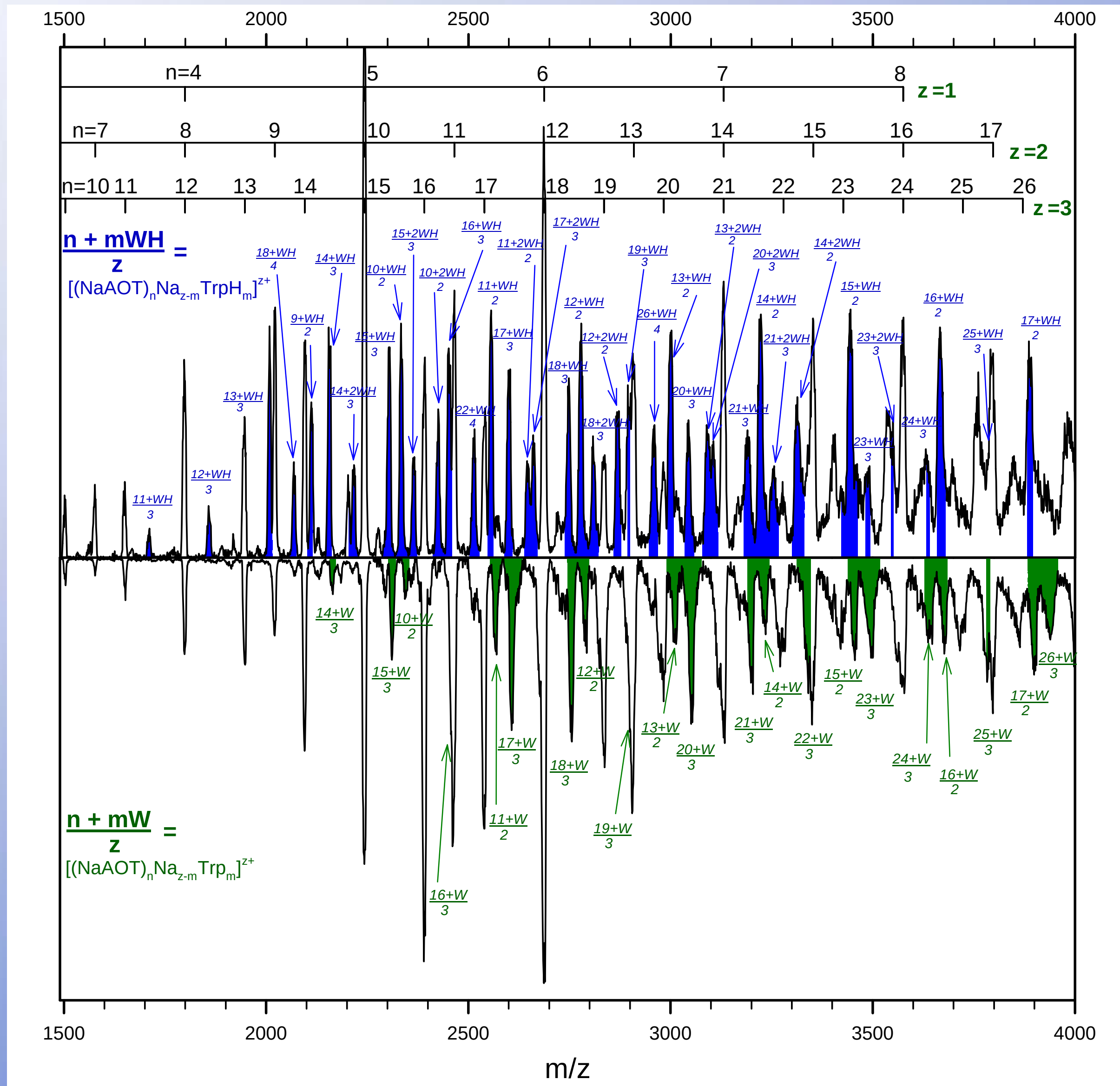
Driving Force for Solubilization in Gas-Phase RM?

Top:

RM occupied with protonated $TrpH^+$

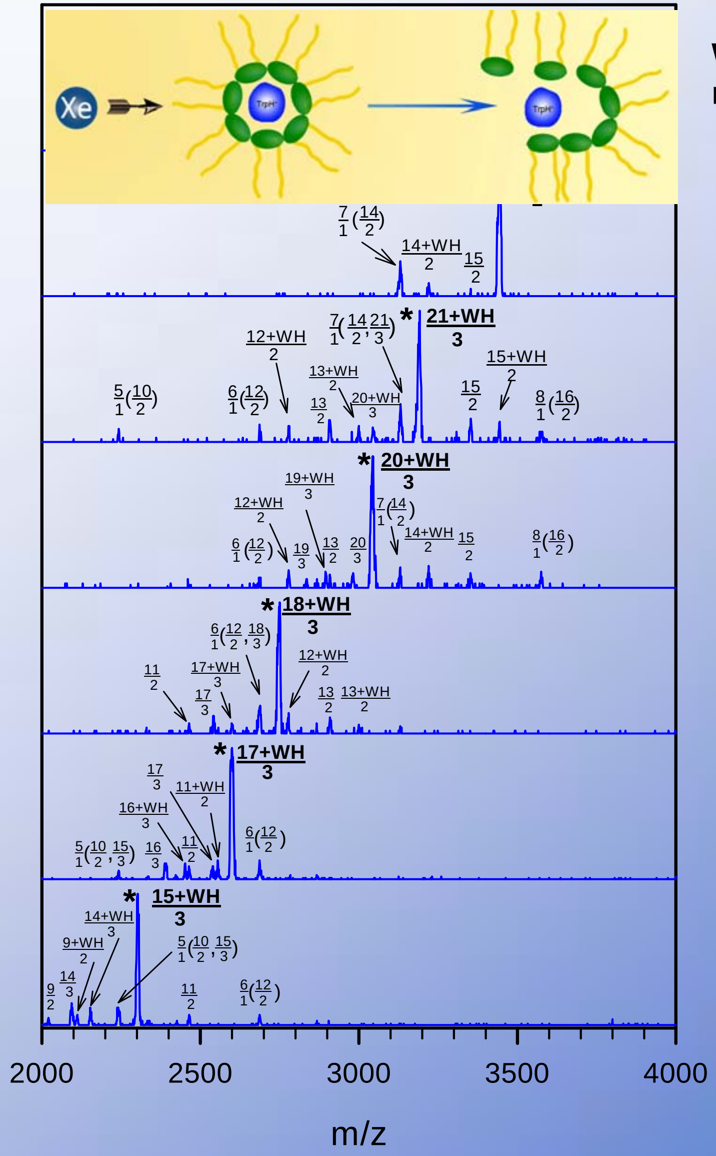
Bottom:

RM occupied with neutral Trp (hydrophobic)

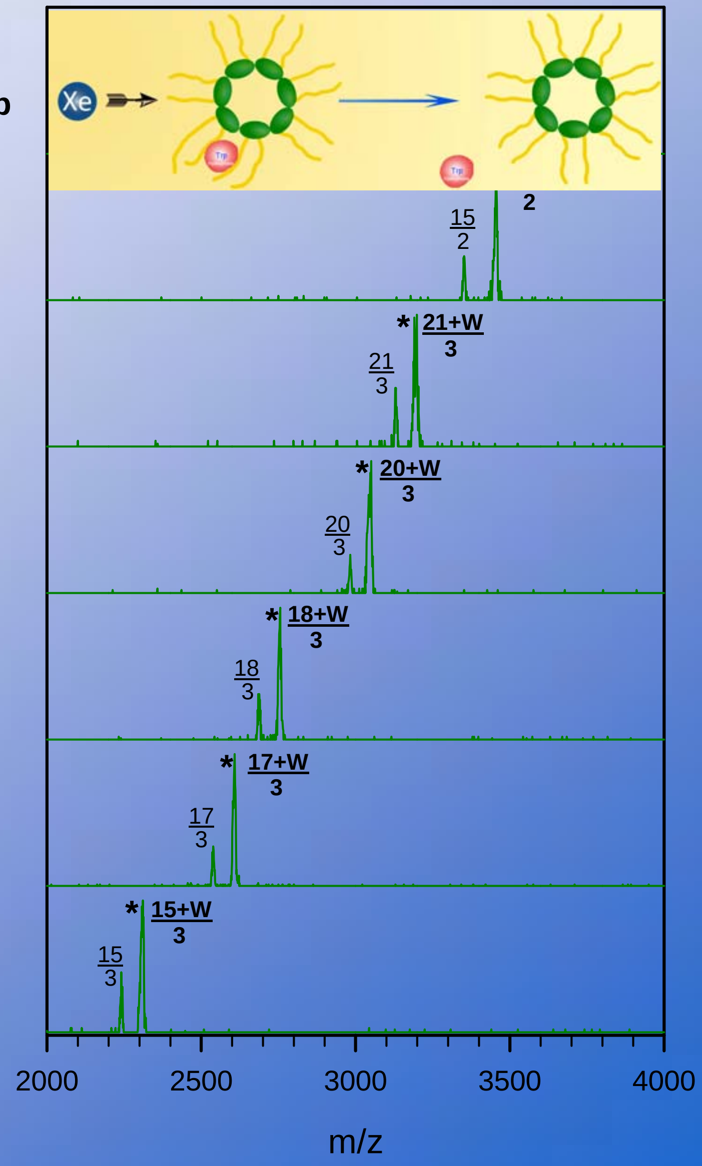


Probing Guest Molecule Location Using CID:
Encapsulation Inside vs. *Attached to the Interface*

WH = $TrpH^+$, protonated Trp



W = Trp, neutral Trp



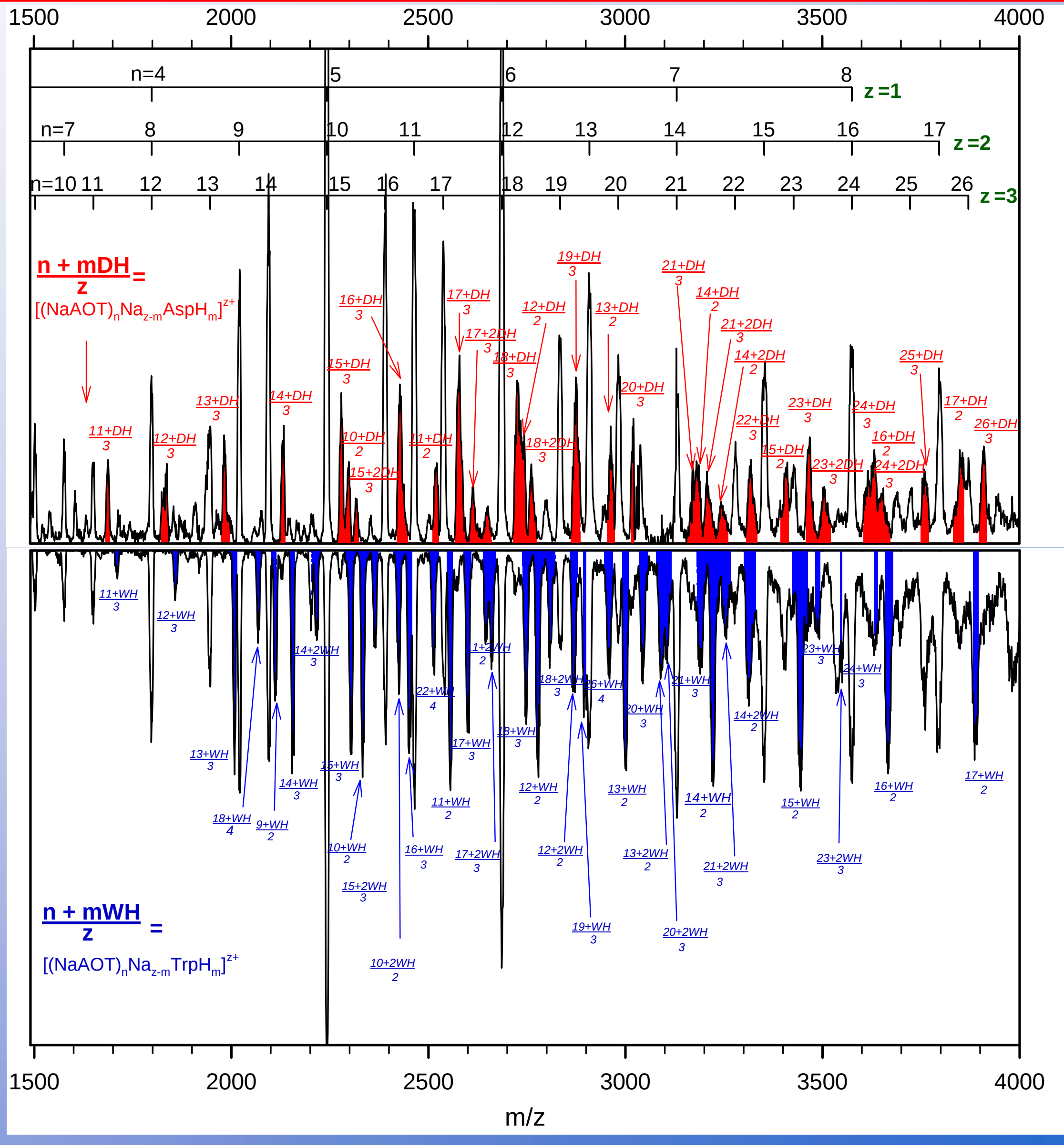
Part III

Selectivity Between Two AAs

Case (1): *Aspartic Acid* vs. *Tryptophan*

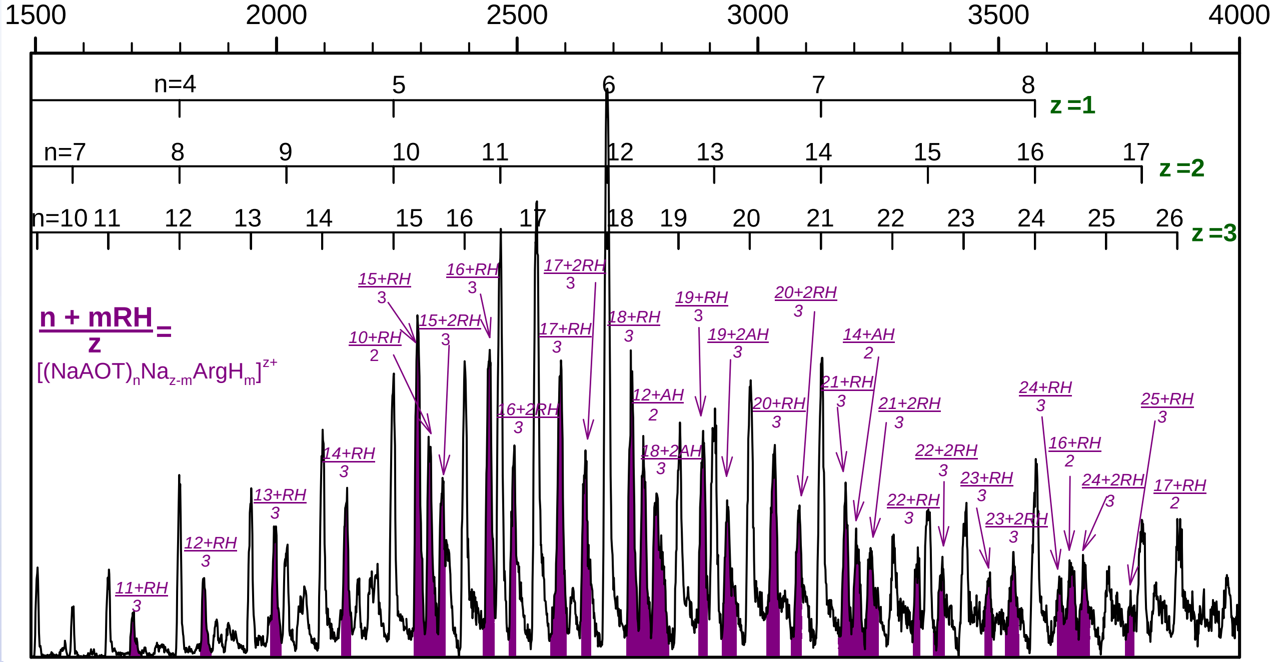
ESI of AOT/Asp

ESI of AOT/Asp+Trp



Case (2): *Arginine* vs. *Tryptophan*

ESI of AOT/Arg



ESI of AOT/Arg+Trp

No changes when mixed with Trp !

Only Arg detected,

no encapsulation of Trp

Fundamentals of Selectivity

	Aspartic acid (D)	Tryptophan (W)	Proline (P)	Arginine (R)
pK_a of α-COOH	1.9	2.8	2.0	2.2
pK_a of α-NH_3^+	9.6	9.4	10.6	9.0
pK_a of acidic R	3.7	-	-	12.5
pI	2.8	5.9	6.3	10.8

pH **of ESI solution of AOT/(Trp + Asp) in methanol/water = 5.1**

pH **of ESI solution of AOT/(Trp + Arg) in methanol/water = 7.4**

Selectivity between different AAs?

- Selectivity reflects a competition between electrostatic and hydrophobic forces, which can be tuned up by changing the pH of ESI solution.
- Amino acid with a higher *pI* exists in protonated form and has a larger affinity with AOT^-

(i.e. Arg > Trp > Asp)

Conclusions

❖ NaAOT surfactants are able to form RM in the gas phase.

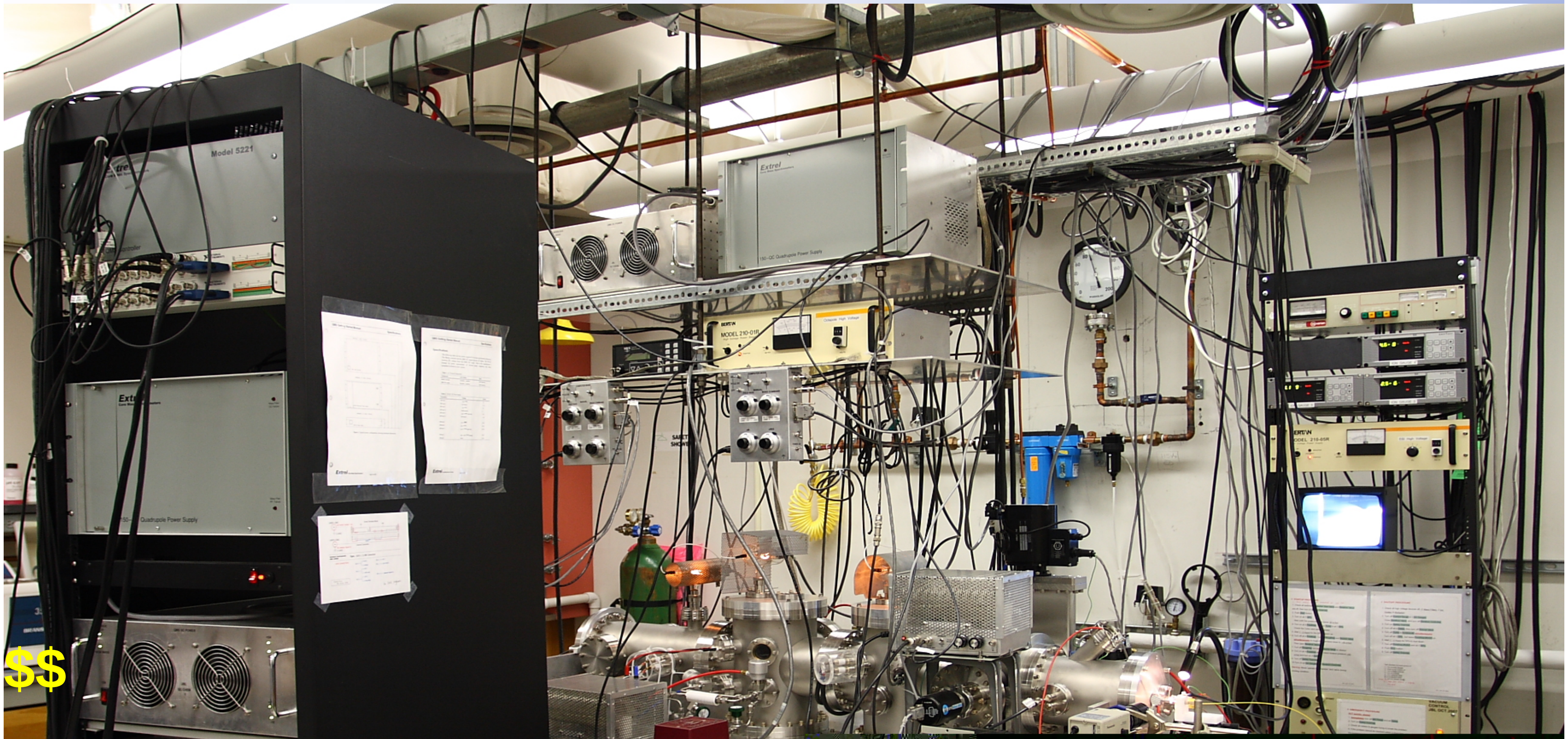
❖ Gas-phase RM can act as nanometer-sized vehicle for selective transport of non-volatile biomolecules into the gas phase.

❖ Driving force for solubilization: electrostatic & hydrophobic interactions.

Application in Analytical Chemistry:

Separation and Direct Determination of ionic and neutral amino acids in solution.

Acknowledgements



$$

ACS-PRF Grant

CUNY Collaboration Grant

QC Research Enhancement Funds