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**On the Arrangement of Ions in Imidazolium-Based Room Temperature Ionic Liquids at the Gas–Liquid Interface, Using Sum Frequency Generation, Surface Potential, and Surface Tension Measurements**

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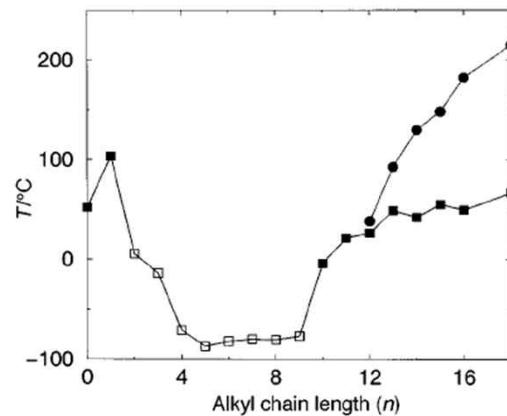
2012.03.09

Presenter: Woongmo Sung

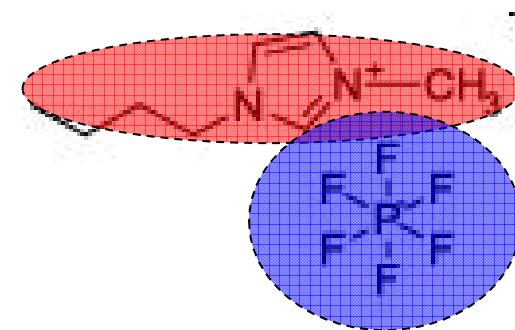
# Room-temperature Ionic liquids

Feature - Coulombic interaction + van der Waals interaction

→ Liquid state in room temperature



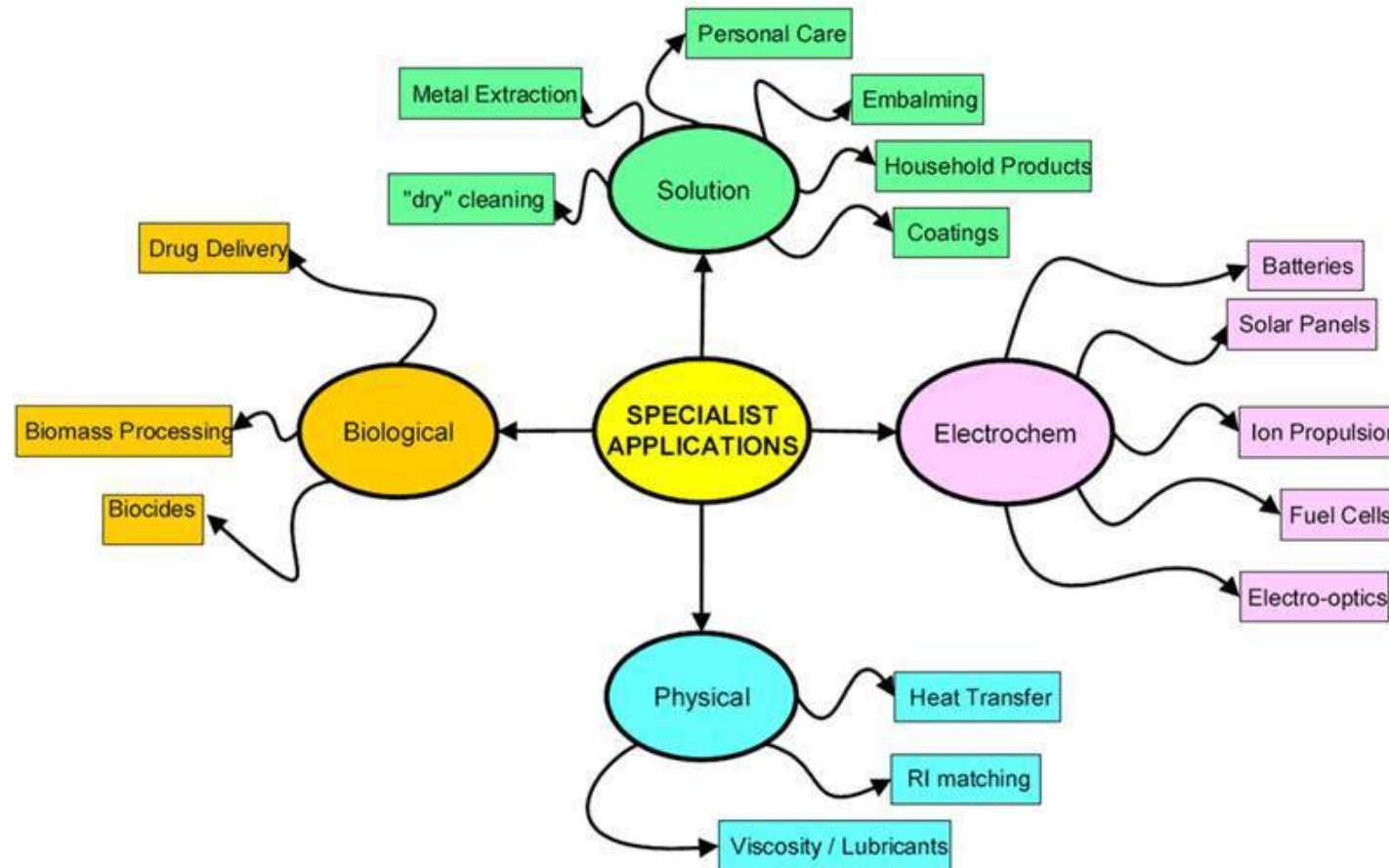
*J. Mater. Chem.* 8, 2627-2636 (1998).



$[BMIM]PF_6$

# Surface structure of ILs

Understanding surface structure of ILs is important for application



# How can we observe??

SFG( $\omega_1 + \omega_2$ )

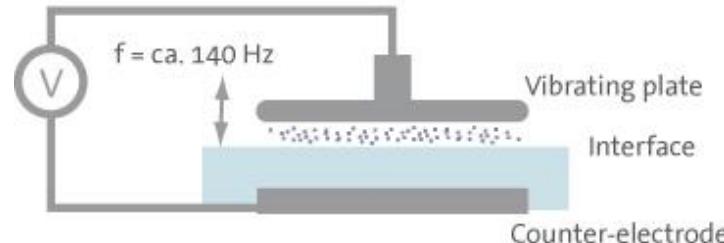
Vis( $\omega_1$ )

IR ( $\omega_2$ )



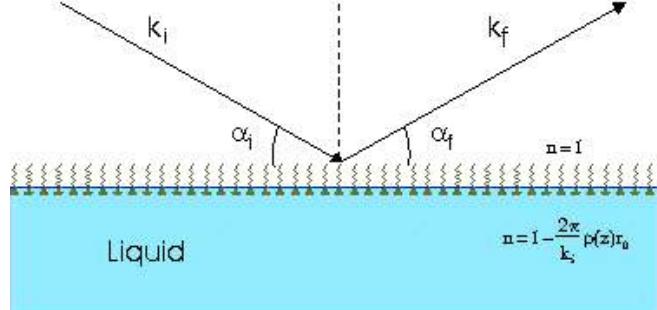
Sum-frequency generation spectroscopy

$$\Delta V = \mu_n / \epsilon \cdot \epsilon_0 \cdot A$$



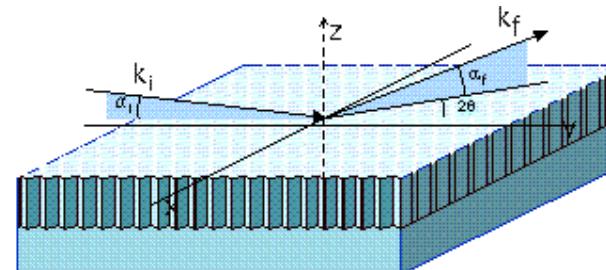
<http://www.ksvnima.com/surface-potential-sensor>

$Q_z$



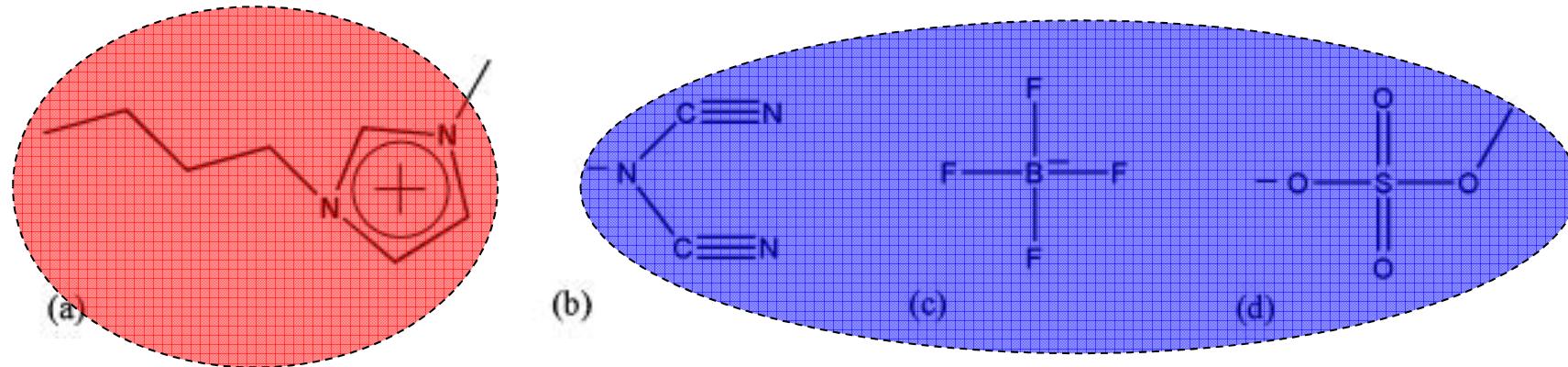
X-ray reflectivity

<http://www.reflec.ameslab.gov/reflectivity.php>



GIXD

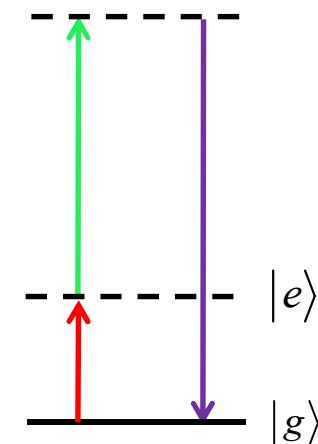
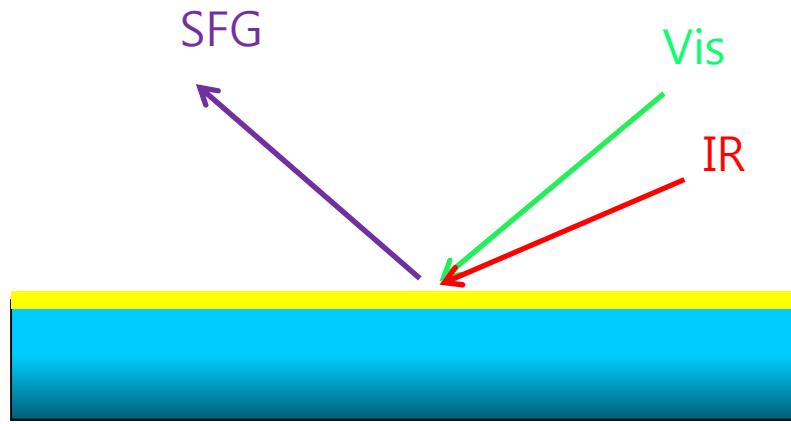
# Materials



**Synthesis and Sample Preparation.** All the materials used for synthesizing the ionic liquids were ACS reagents purchased from Aldrich, except for the sodium dicyanamide, which was from Alfa-Aesar. The water used was deionized with a Millipore

# SFG spectroscopy

## 1) Basic principles



$$I(\omega_{SFG} = \omega_{IR} + \omega_{VIS}) \propto |\chi_{eff}^{(2)} E(\omega_{IR}) E(\omega_{VIS})|^2$$

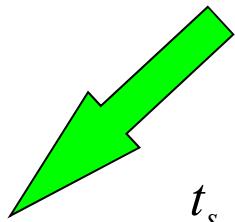
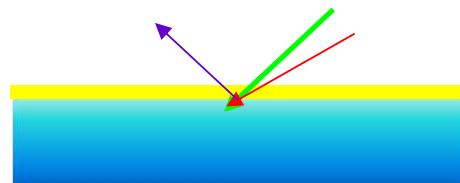
$$\chi_{eff}^{(2)} = [i \cdot \hat{L}(\omega_{SFG})] \cdot \chi^{(2)} [\hat{j} \cdot \hat{L}(\omega_{VIS})] [\hat{k} \cdot \hat{L}(\omega_{IR})]$$

# SFG spectroscopy

$$\chi_{eff}^{(2)} = [i \cdot \hat{L}(\omega_{SFG})] \cdot \chi^{(2)} [j \cdot \hat{L}(\omega_{VIS})] [\hat{k} \cdot \hat{L}(\omega_{IR})]$$

$$L(\omega) = \begin{bmatrix} L_{xx}(\omega) & 0 & 0 \\ 0 & L_{yy}(\omega) & 0 \\ 0 & 0 & L_{zz}(\omega) \end{bmatrix}$$

Just think about Fresnel coefficient



$$t_s = E_s''(\omega) / E_s(\omega) = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2}$$

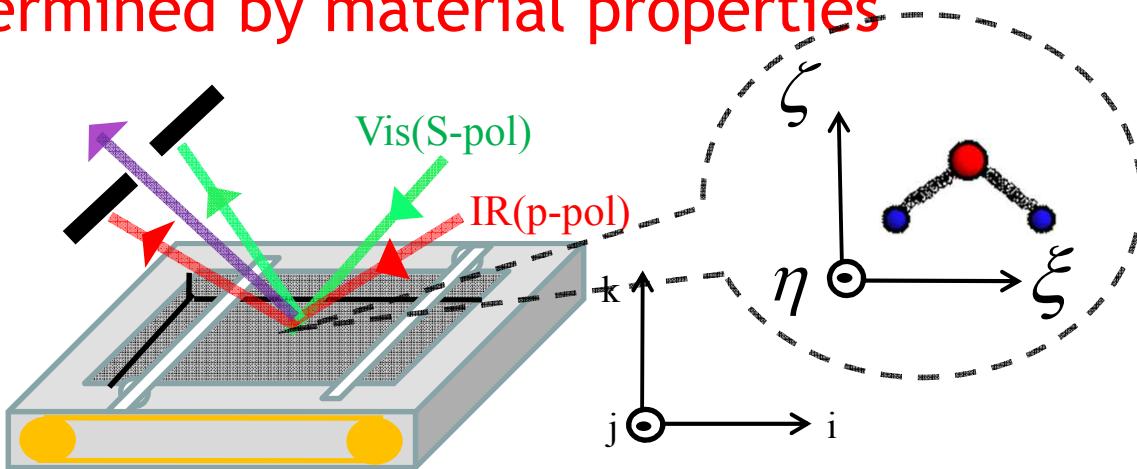
$$t_p = E_p''(\omega) / E_p(\omega) = \frac{2n_1 \cos \theta_1}{n_2 \cos \theta_1 + n_1 \cos \theta_2}$$

# SFG spectroscopy

$$\chi_{eff}^{(2)} = [\hat{i} \cdot L(\omega_{SFG})] \cdot \hat{\chi}^{(2)} [\hat{j} \cdot L(\omega_{VIS})] [\hat{k} \cdot L(\omega_{IR})]$$



Determined by material properties



$$\chi_{ijk}^{(2)} = N_s \sum_{\xi, \eta, \zeta} \alpha_{\xi \eta \zeta}^{(2)} \langle \hat{(\xi \cdot i)} \hat{(\eta \cdot j)} \hat{(\zeta \cdot k)} \rangle$$

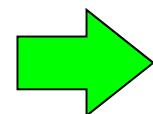
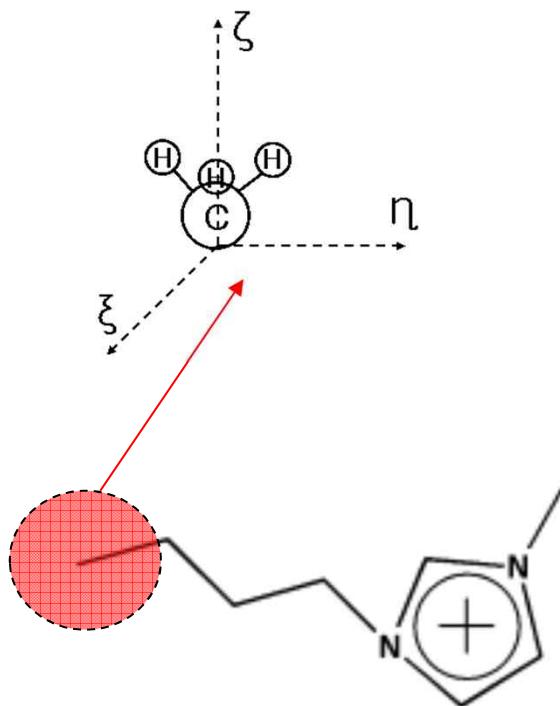
Information about  
molecular orientation

$$\alpha_{\xi \eta \zeta}^{(2)} = \alpha_{NR}^{(2)} + \sum_q \frac{\alpha_{q, \xi \eta \zeta}}{\omega_{IR} - \omega_q + i\Gamma_q}$$

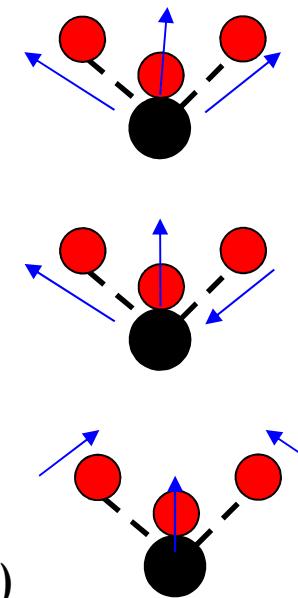
Intrinsic property of molecule

# SFG spectroscopy

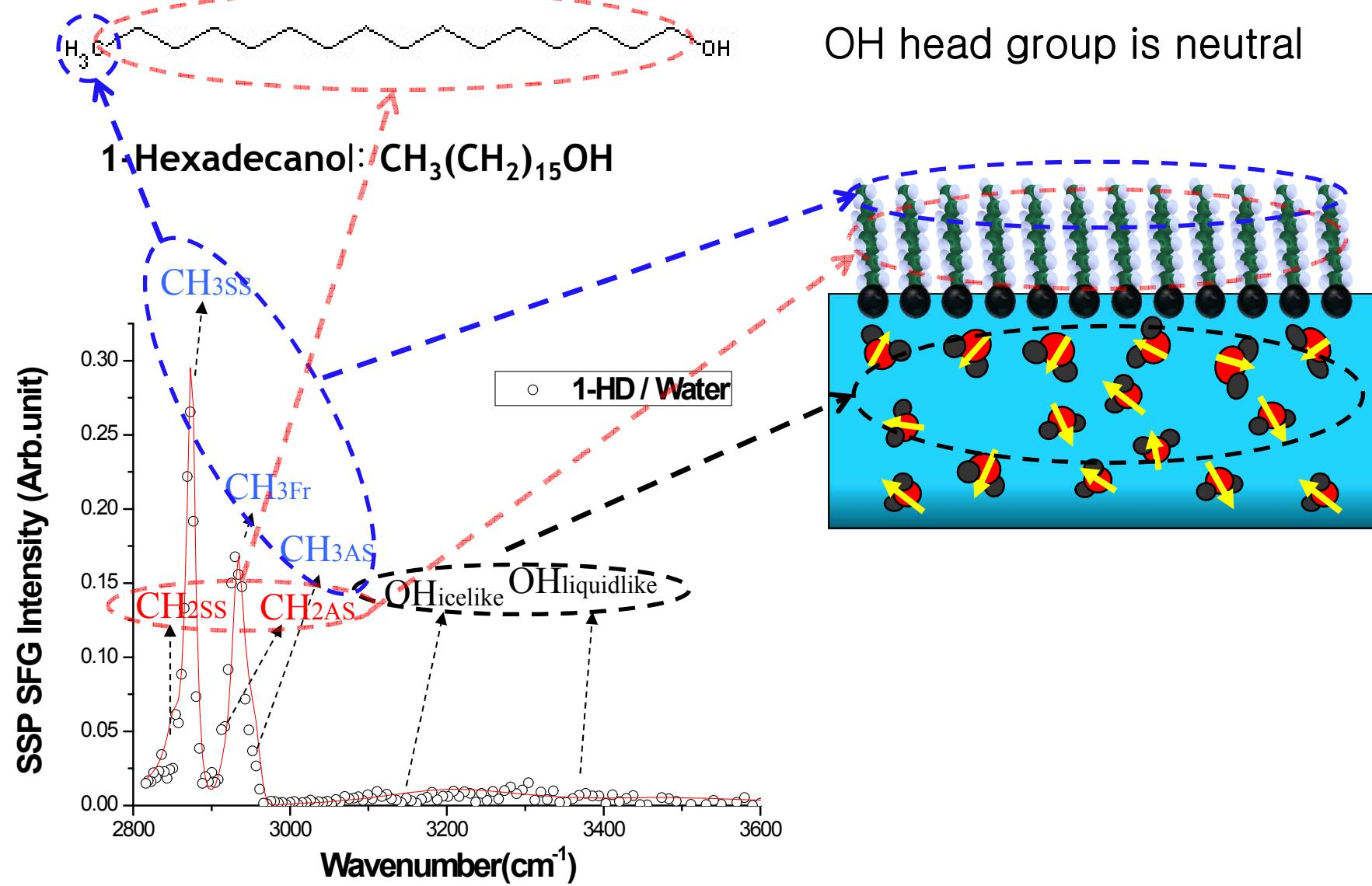
2) Analysis of  $\text{CH}_3$  vibrational modes ( $2800\text{--}3000\text{cm}^{-1}$ )



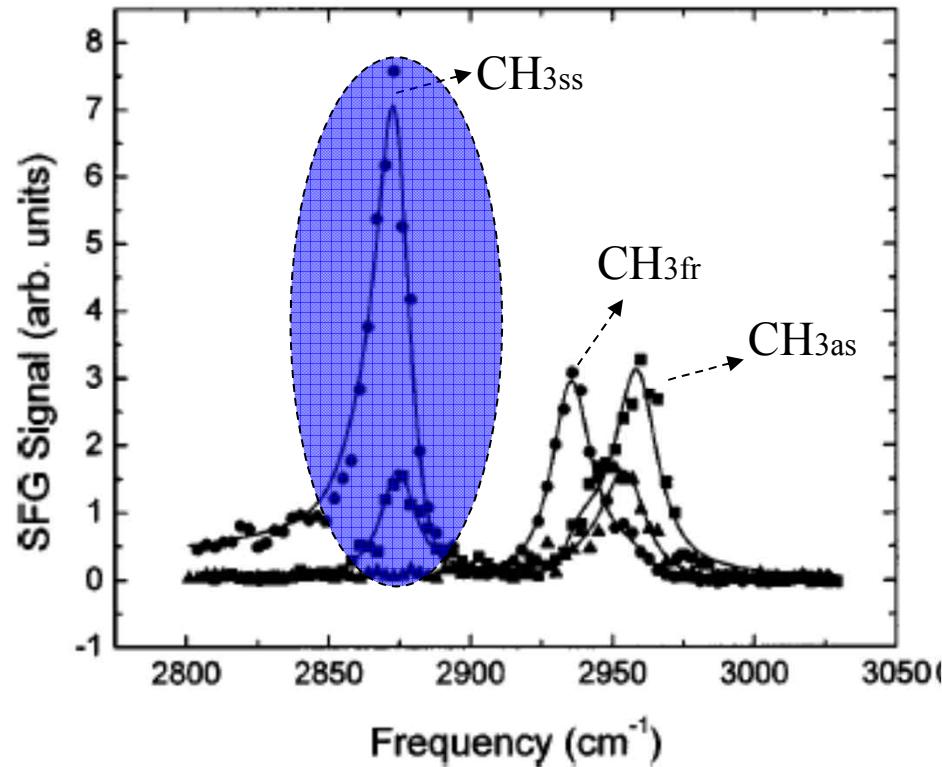
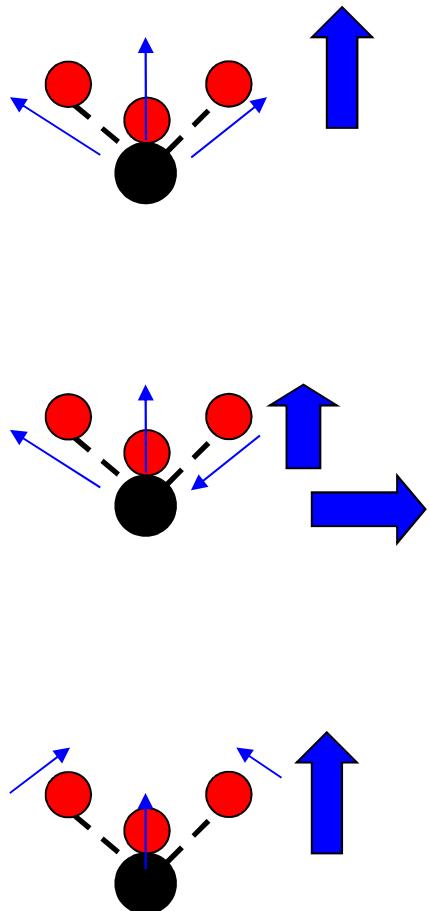
- 1)  $\text{CH}_3$  symmetric stretch
- 2)  $\text{CH}_3$  asymmetric
- 3)  $\text{CH}_3$  Fermi resonance  
(of bending overtone)



# Experimental result (Reference sample)



# Experimental result (Reference sample)



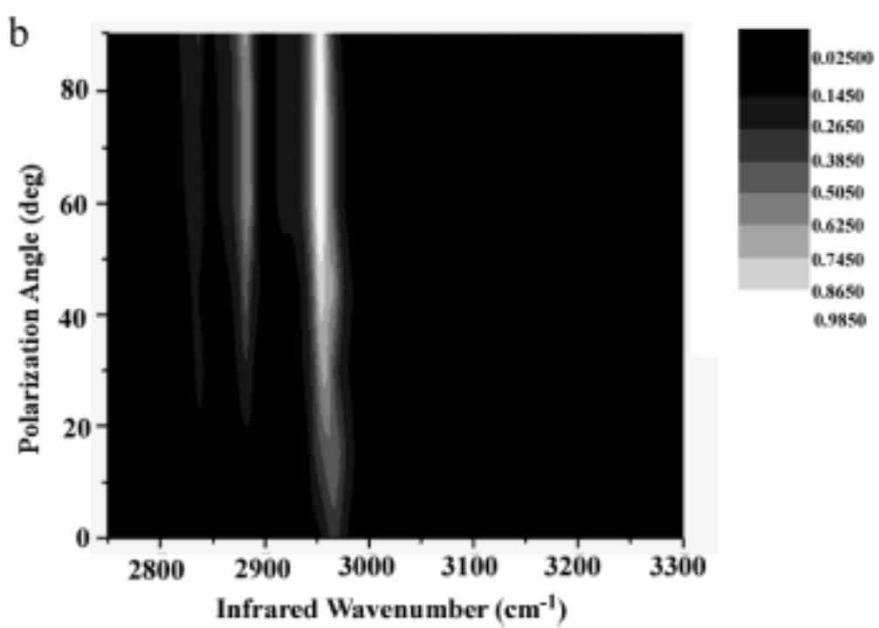
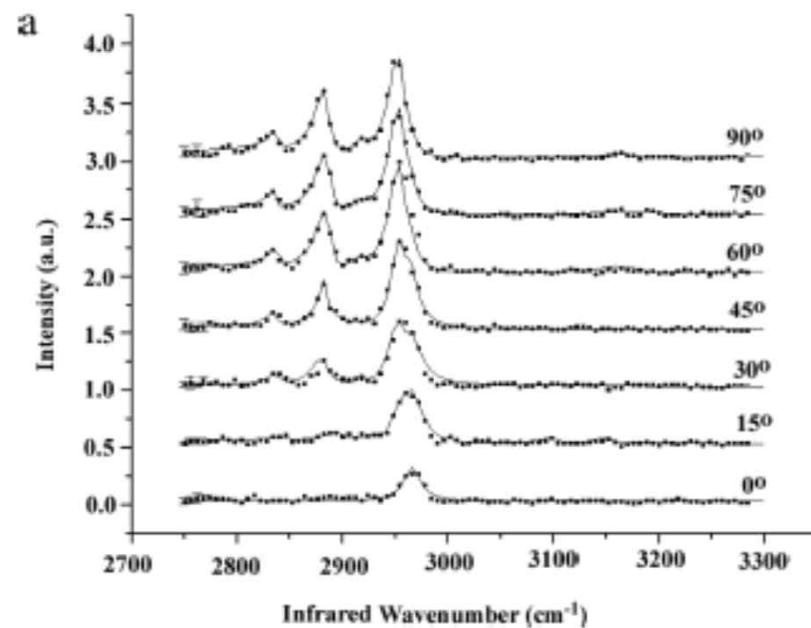
$$\frac{\chi_{\text{eff}, \text{ppp}}^{(2)}}{\chi_{\text{eff}, \text{ssp}}^{(2)}} = 0.021 \frac{\sin^2 \theta (1-r)}{\sin^2 \theta + r(1+\cos^2 \theta)} + \frac{1.914}{(n')^4} \frac{r \sin^2 \theta + \cos^2 \theta}{\sin^2 \theta + r(1+\cos^2 \theta)} - 0.766, r = 2.2$$

# Experimental result [BMIM]MS

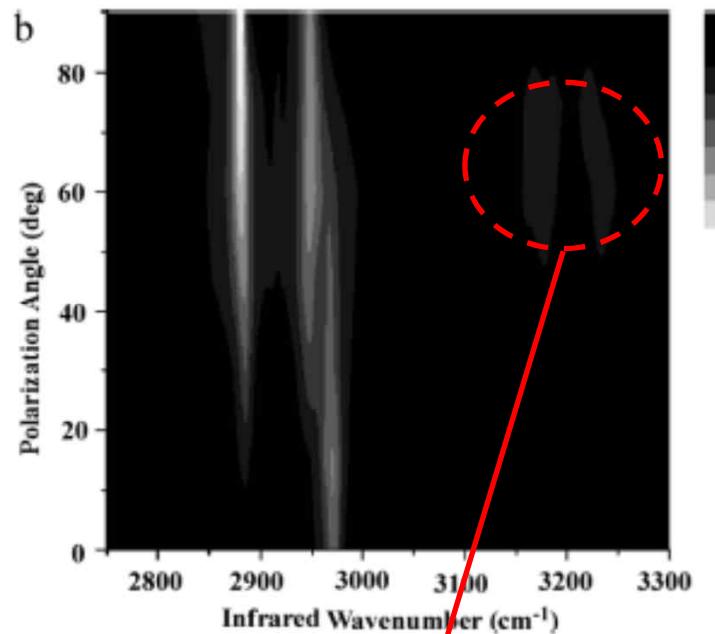
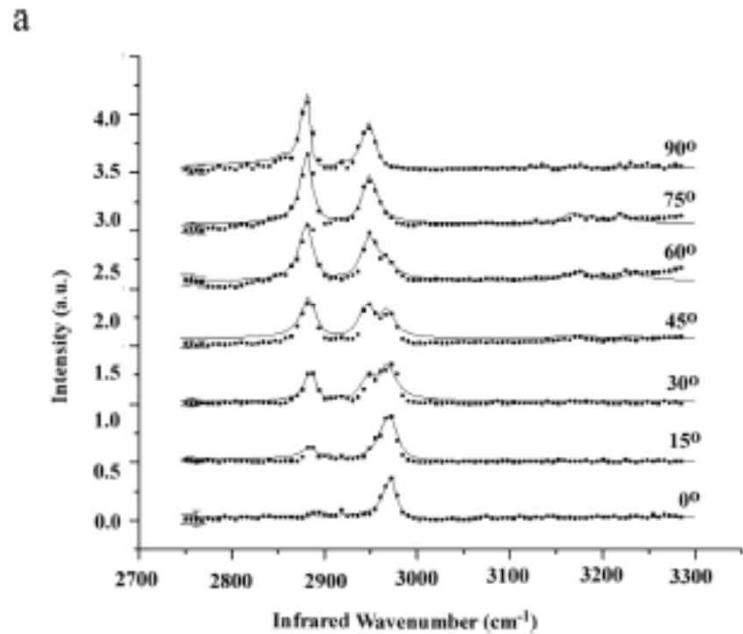
## Polarization configuration

: SFG - rotate 15° / VIS - 45° / IR - 0° (purely P-pol)

$$I(\omega_{SF})\alpha|P^{(2)}|^2 = \left| \chi_{\text{eff},ssp}^{(2)} \sin \sigma_s + \chi_{\text{eff},ppp}^{(2)} \cos \sigma_s \right|^2 \quad (15)$$

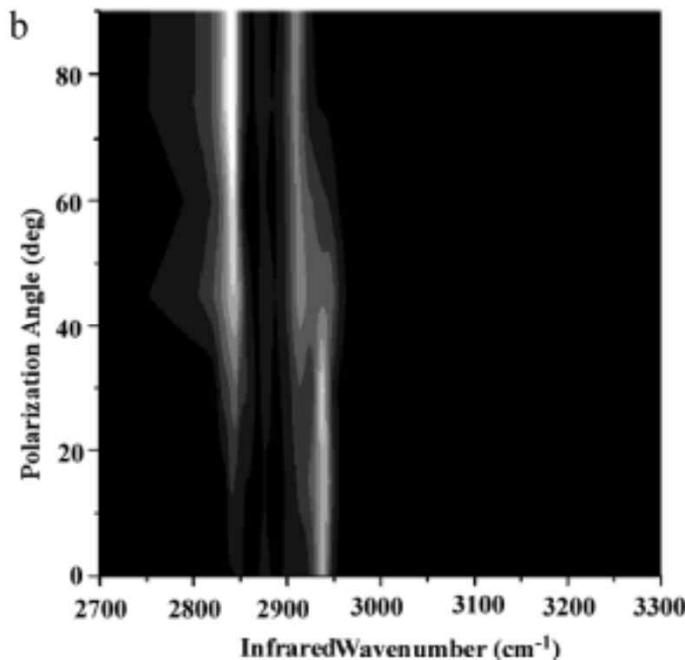
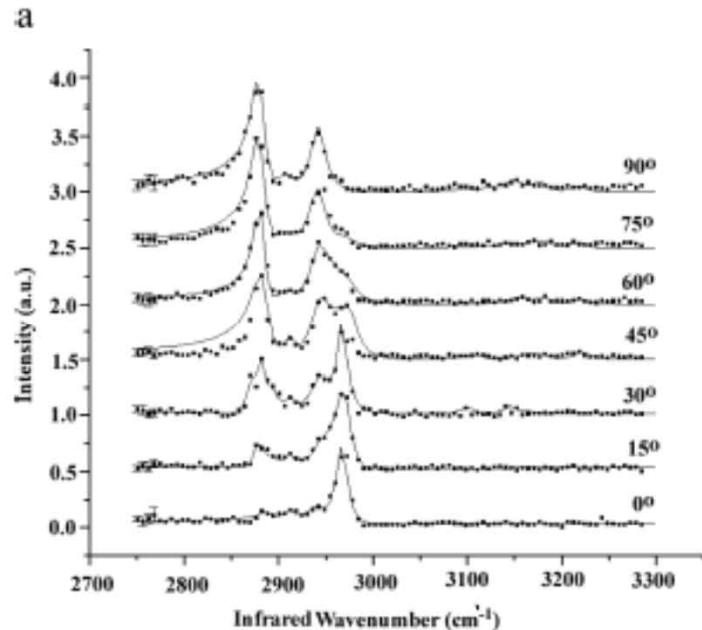


# Experimental result [BMIM]BF<sub>4</sub>



Assigned as H-C(4) C(5)-H  
Symmetric and asymmetric stretch modes

# Experimental result [BMIM]DCA



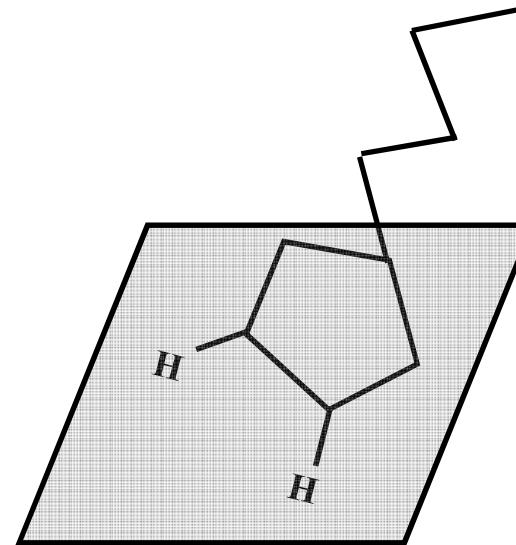
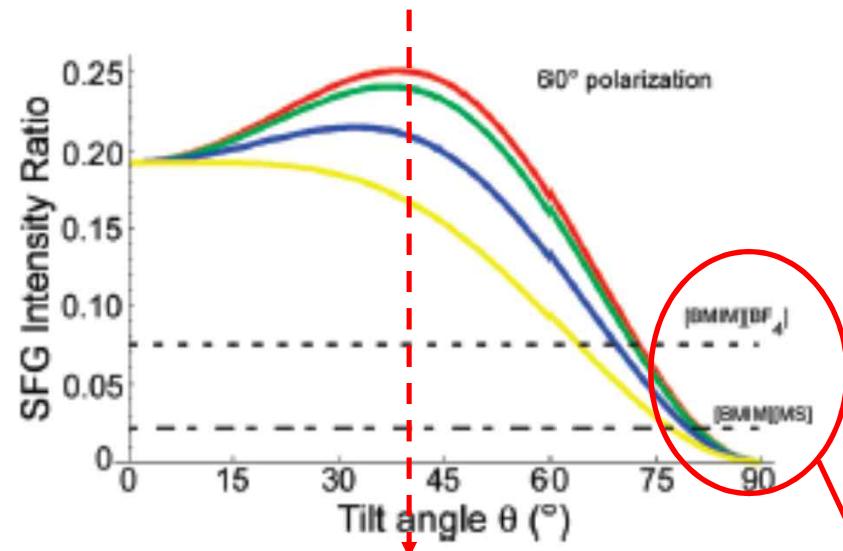
From simultaneous  
fitting of spectra



TABLE 3: Values Used for the Estimation of Surface Potential on the Surface

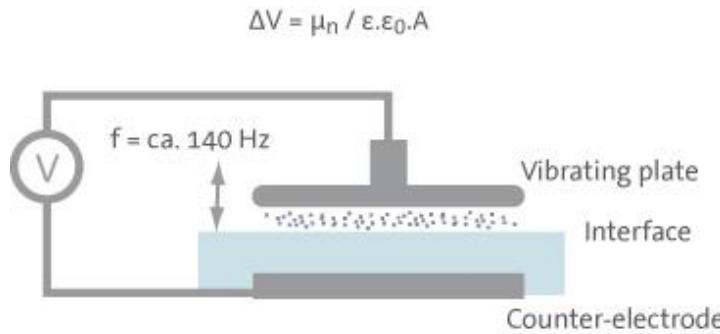
IL	$\varepsilon_t$	$\mu_c$ (D)	$\theta_c$ (deg)	$\theta_a$ (deg)	$\delta_{s,\max}$ ( $\text{\AA}$ )	$\varepsilon_s$	$A_c$ ( $\text{\AA}^2$ )	$A_u$ ( $\text{\AA}^2$ )
[BMIM][BF <sub>4</sub> ]	2	0.38	47		3.27	11.7 <sup>70</sup>	22.25 <sup>71</sup>	19.63 <sup>72,73</sup>
[BMIM][DCA]	2	0.38	47	70	3.57	11.3 <sup>74</sup>	22.25	24.63 <sup>72,73</sup>
[BMIM][MS]	2	0.38	45	65 <sup>12</sup>	3.65	14.8 <sup>75</sup>	22.25	26.06 <sup>71,76,77</sup>

# Experimental result



From calculation, it was found that imidazolium ring is almost parallel to the surface!?

# Experimental result (surface potential)

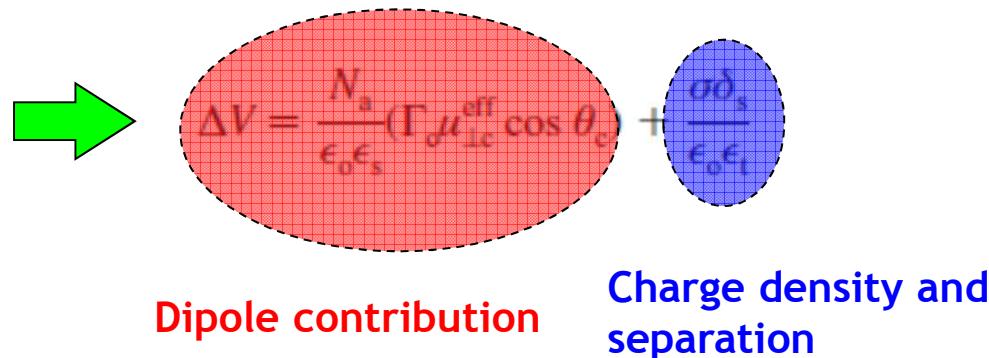


$$\frac{dQ}{dt} = U \cdot \epsilon \epsilon_o \frac{d}{dt} \left( \frac{1}{D(t)} \right)$$

$$I = U \cdot \frac{dC}{dt} = -U \cdot \epsilon \epsilon_o A \cdot \frac{D_1 \omega \cos(\omega t)}{[D_o + D_1 \sin(\omega t)]^2}$$

$$\Delta V = N_a \Gamma_s \frac{\mu_{\perp}^{\text{eff}}}{\epsilon_0 \epsilon_t} (\Gamma_s) + \frac{\sigma \delta_s}{\epsilon_0 \epsilon_s} + \frac{2kT}{e} \sinh^{-1} \left( \frac{\sigma e}{2\epsilon_0 \epsilon_s k T \kappa} \right) \quad (5)$$

Since ILs consist of only ions, neglect diffusion double layer



# Experimental result (surface potential)

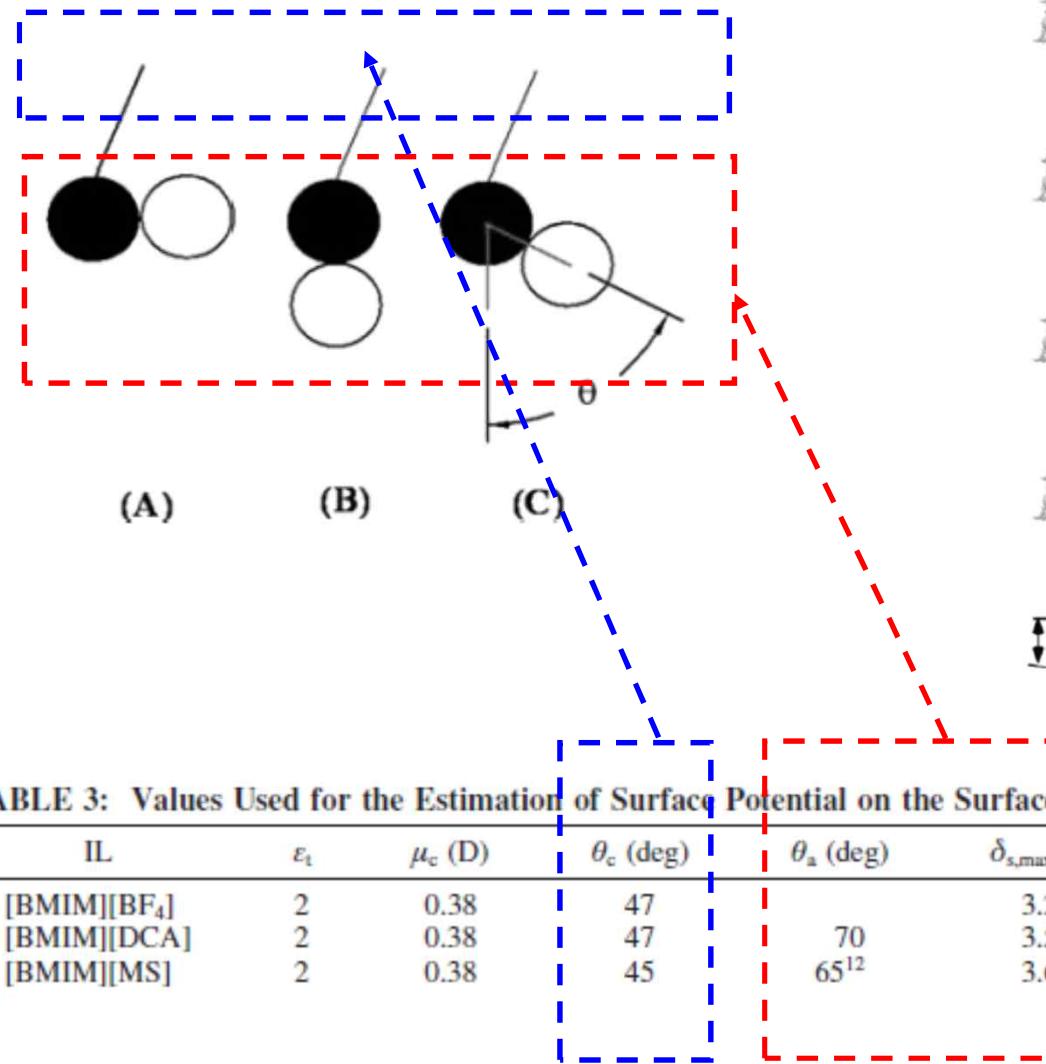


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# Conclusion

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- 1) Interfacial structure of room-temp ILs was studied by SFG and surface potential measurement....
- 2) From SFG polarization mapping method, orientation angle of terminal methyl group and imidazolium ring were obtained.....
- 3) From surface potential measurement, anions are placed almost next to cations....