



Sum-frequency generation spectroscopy study of an Ionic liquid at a Graphene-BaF₂ (111) interface

S. Xu, S. Xing, S.-S. Pei, S. Baldelli, *J. Phys. Chem. B*, **118**, 5203-5210 (2014)

2014. 09. 06.

Jonggwan Lee

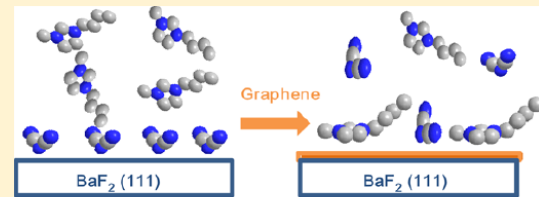
Soft-matter optical spectroscopy Lab.

Dept. of Physics, Sogang University



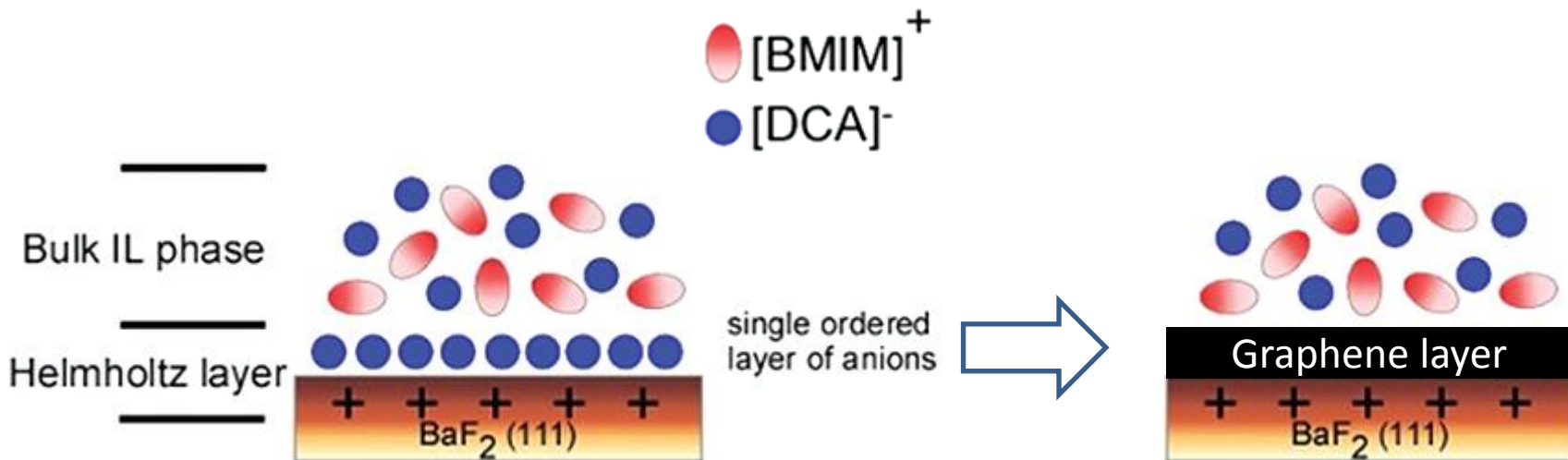
Abstract

ABSTRACT: Sum frequency generation (SFG) vibrational spectroscopy and contact angle measurements of an ionic liquid, 1-butyl-3-methylimidazolium dicyanamide [BMIM][DCA], at solid–liquid interfaces are reported. Bare solid single crystal BaF_2 (111) surface, a single and few layer graphene-coated BaF_2 (111) surface are used as the solid substrates. The SFG results indicate that both $[\text{BMIM}]^+$ and $[\text{DCA}]^-$ can be detected specifically on the graphene-coated BaF_2 (111) surface, without coating only $[\text{DCA}]^-$ are observed. $[\text{DCA}]^-$ anions are attracted to the positively charged BaF_2 (111) surface and occupy the first layer at the solid–liquid interface. The graphene coating shields the charged crystal surface and allows both cations and anions to exist at the interface. Furthermore, increase in the contact angle of BaF_2 surface after graphene layers deposition suggests that the graphene coating lowers the surface energy.





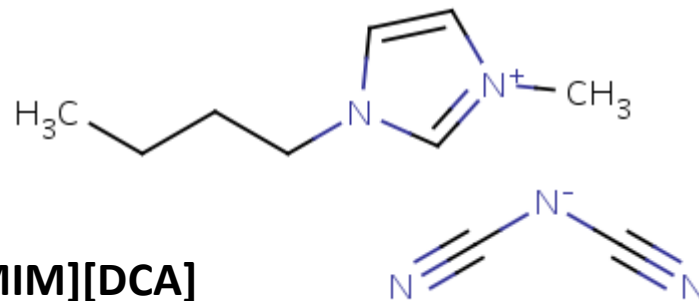
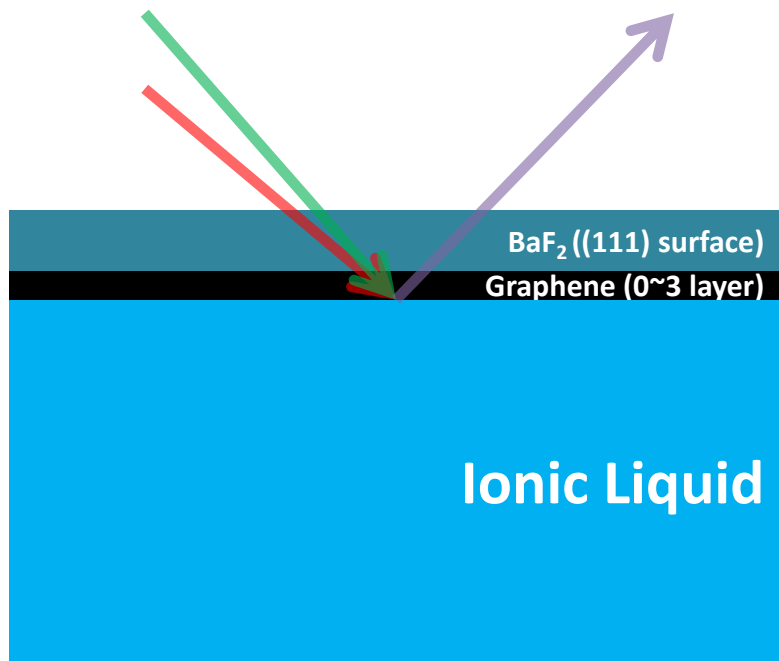
Motivation



C. Y. Peñalber, S. Baldelli, *J. Phys. Chem. Lett.* **3**, 844-847 (2012)



Experimental

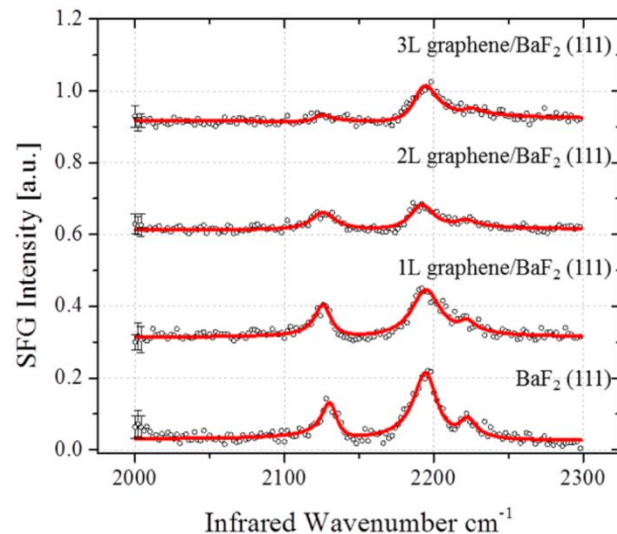
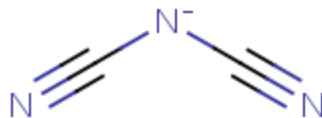
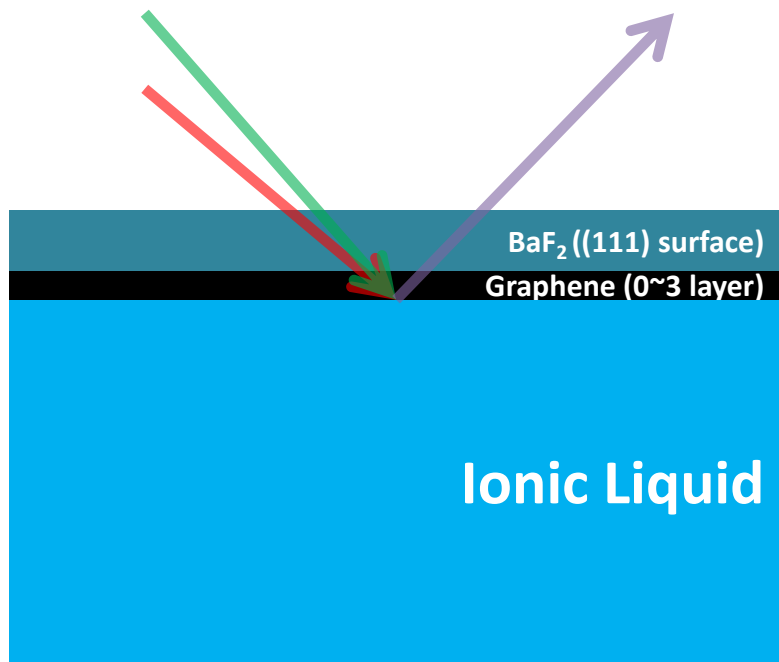


[BMIM][DCA]

1-butyl-3-methylimidazolium dicyanamide



Results – SFG spectrum (CN range)

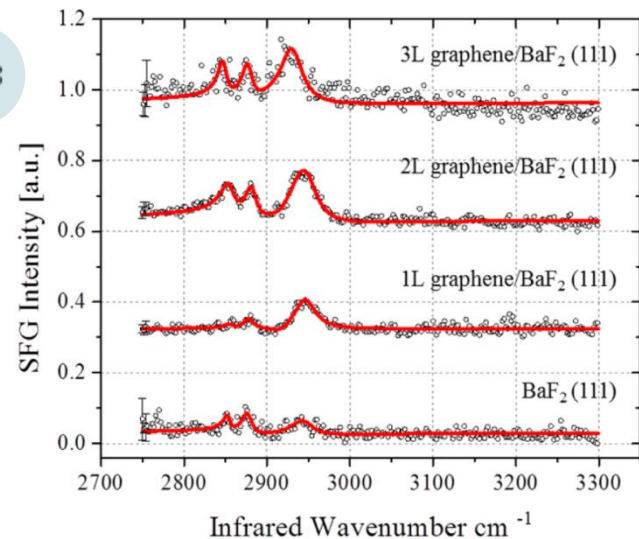
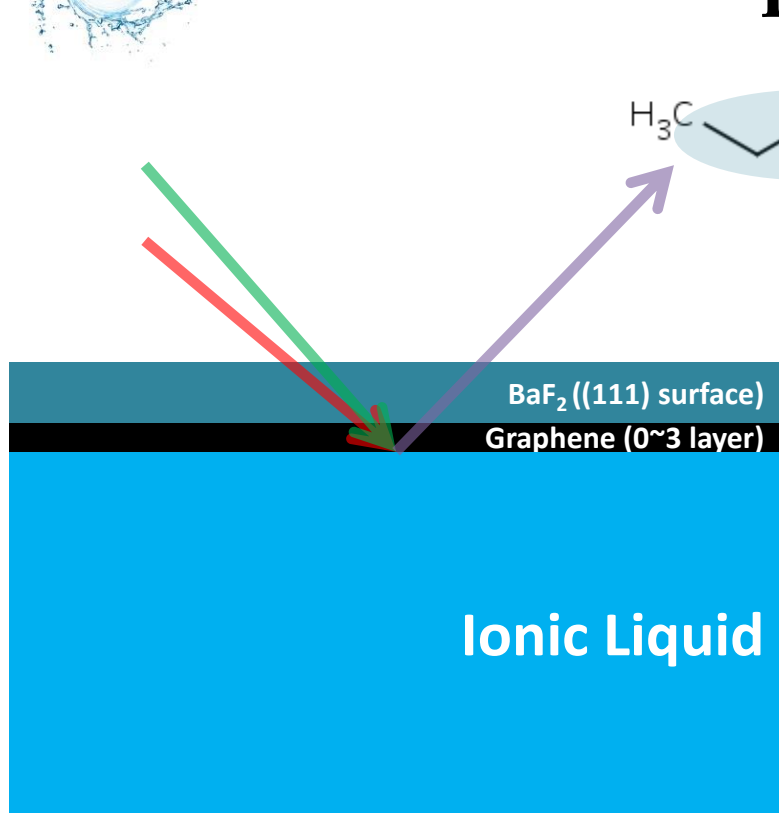


The CN vibrational mode response **decreased** with incrementing graphene layers.

Surface adsorption of [DCA]⁻ anion decreases with graphene layers



Results – SFG spectrum (CH range)

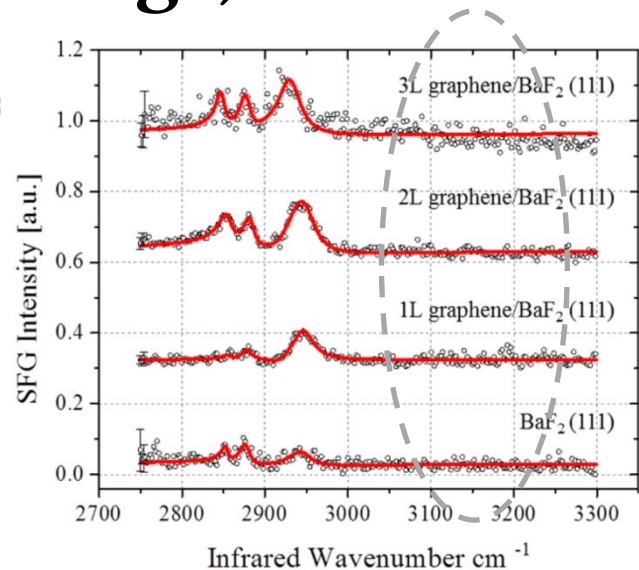
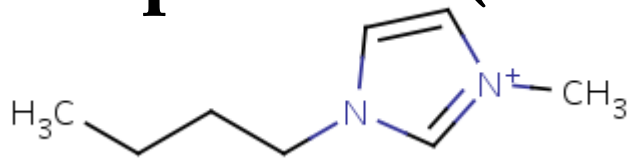
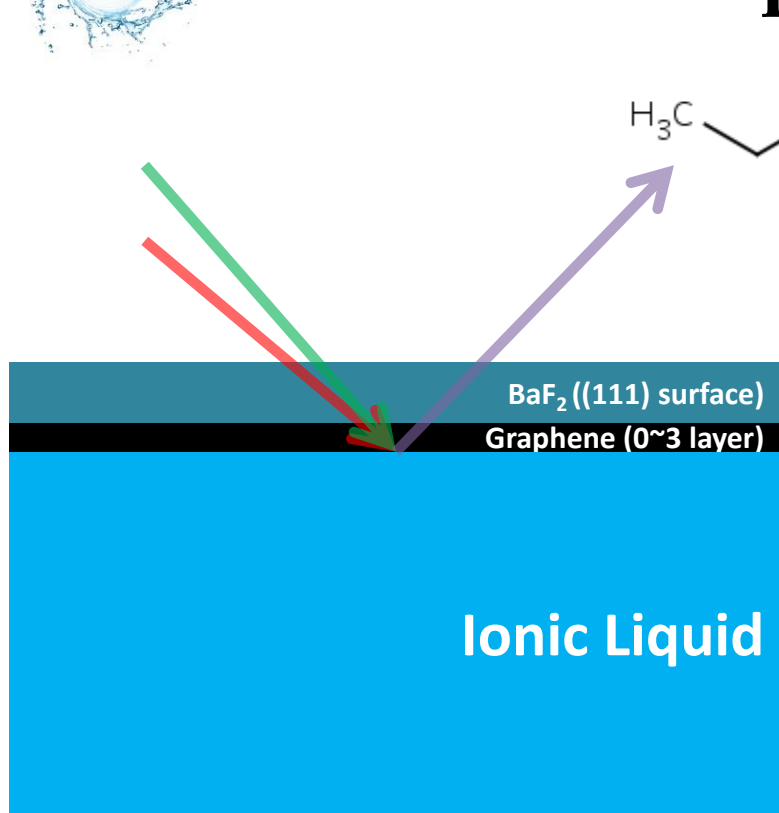


The CH vibrational mode response **increased** with incrementing graphene layers.

Surface adsorption of [BMIM]⁺ cation increases with graphene layers



Results – SFG spectrum (CH range)



Imidazolium ring vibrational modes ($\sim 3150\text{cm}^{-1}$)
are not observed in spectra

Preferential orientation of imidazolium rings
in the top layer is parallel to the surface.



Results – Contact angle measurement

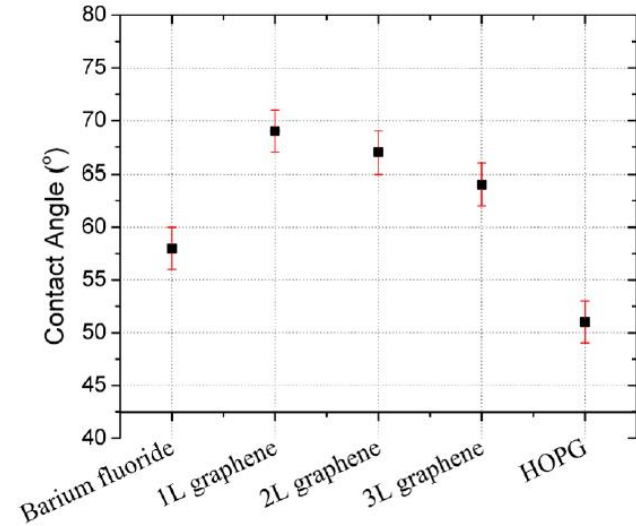
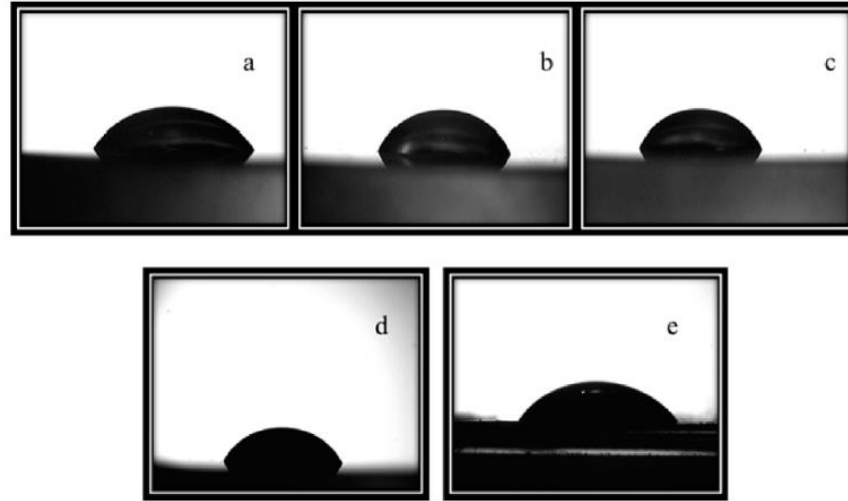


Figure 3. Contact angle of [BMIM][DCA] on (a) bare BaF₂ (111) surface, (b) monolayer graphene-coated BaF₂ (111) surface, (c) bilayer graphene-coated BaF₂ (111) surface, (d) triple-layer graphene-coated BaF₂ (111) surface, and (e) HOPG surface.

HOPG : High-ordered pyrolytic graphite



Conclusion

Ionic liquid [BMIM][DCA] at $\text{BaF}_2(111)$ /graphene/ionic liquid interface was studied with sum-frequency generation spectroscopy

The results show that only $[\text{DCA}]^-$ is observed at the bare $\text{BaF}_2(111)$ surface, and both $[\text{BMIM}]^+$ and $[\text{DCA}]^-$ are detected at the graphene-coated $\text{BaF}_2(111)$ surface. (Graphene layer shields the charged crystal surface)

Furthermore, contact angle results showed that the graphene-coated surface is more hydrophobic than the bare BaF_2