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## Sum frequency generation study on the orientation of room-temperature ionic liquid at the graphene–ionic liquid interface

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## ABSTRACT

The sum frequency generation (SFG) vibrational spectrum and contact angle of a room-temperature ionic liquid, 1-butyl-3-methylimidazolium methane sulfate, [BMIM][MS], at the graphene interface has been measured. The SFG spectra are dominated by the CH<sub>3</sub> resonance of the anion. The methyl group of methane sulfate is oriented at an angle greater than 40° from the surface normal. The SFG data suggests the cation, [BMIM]<sup>+</sup>, is weakly oriented with the alkyl chain parallel to the graphene plane and the aromatic ring somewhat tilted from the surface plane. As the ionic liquid [BMIM][MS] wets the surface with a contact angle of 58 ± 2°, suggesting that the non-polar interaction of the alkyl chain and π–π interaction of the ring, to graphene dominate the surface interactions.

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Although pioneering work on graphene was awarded the 2010 Nobel Prize in physics [1], there are still many areas of its chemistry in need of exploration. This is especially true of its surface chemistry, since many of the applications envisioned for graphene involve surface interactions [2]. In the realm of energy systems for graphene such as dye-sensitized solar cells and super capacitors, room-temperature ionic liquids are considered the medium of choice. Thus, while the ionic liquid appears to be a promising medium, there is almost no molecular-level information as to their interaction with the solid graphene surface.

Detailed experimental molecular information on the surface chemistry of graphene is limited however recent simulations have been conducted on the interaction of ion pair with the free graphene-like layer. The simulation indicates a specific orientation of the ion pair to the graphene face is preferred and that there is partial charge transfer between the ions and the graphene suggesting a relatively strong interaction [3]. Nonlinear optics of the graphene substrate has been performed using second harmonic generation (SHG) where the rotation around the surface normal produced an anisotropic SHG signal. Surface symmetry of the graphene, threefold, dominated over the fourfold symmetry of the substrate [4].

The interfacial interaction of the ionic liquid 1-butyl-3-methylimidazolium methyl sulfate, [BMIM][MS], with a graphene surface is studied using sum frequency generation vibrational spectroscopy and contact angle measurements. The results suggest a significant interaction of the ionic liquid dominated by anion adsorption.

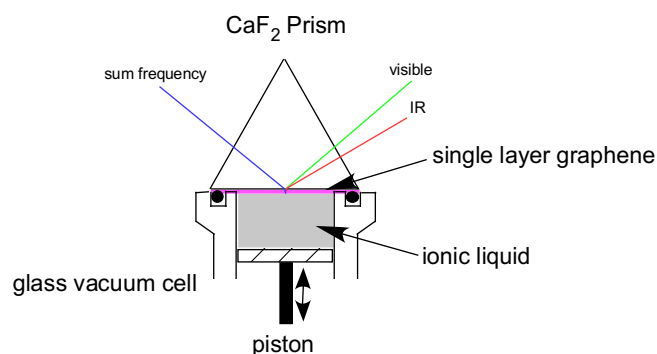
The cation interacts with graphene where the alkyl chains are extended parallel to the surface and the imidazolium ring is slightly tilted to the surface plane of graphene. This arrangement of the ionic liquid is much different than for other solid surfaces [5–7] possibly due to strong binding of the anion and the possibility for π–π interactions between imidazolium and graphene.

A single-layer graphene sample is prepared by chemical vapor deposition on a copper substrate in a quartz tube furnace at ambient pressure. The Cu is dissolved and the graphene transferred to the CaF<sub>2</sub> prism substrate [8]. Graphene appeared to be well adhered to the substrate as sonication in various solvents was unable to remove it by visual inspection. Ionic liquid, [BMIM][MS] has been synthesized and purified by previous published procedures [9–11]. The compound contains less than 10 ppm Cl<sup>−</sup> (by ion selective electrode) and water partial pressure is <10<sup>−7</sup> Torr (by mass spectrometry). The ionic liquid sample is introduced, without air contact, into a vacuum tight glass cell and bulk liquid is in contact with the graphene sample, see Figure 1. The graphene layer is at the surface of an equilateral CaF<sub>2</sub> prism. Infrared and 532 nm visible laser beams are overlapped (through the prism) at the solid–liquid interface with beam energy densities of 10 and 5 mJ/cm<sup>2</sup>, respectively to avoid damage to the graphene layer. At energy density 10× higher the graphene is visibly damaged over the course of 2 h. The experiment is made possible by graphene's high and near uniform transparency over a wide range of the optical spectrum.

Sum frequency generation, SFG, is a second order nonlinear process where signal is generated from molecules in a non-centrosymmetric environment, such as the surface [12]. This process is described by the second-order susceptibility.

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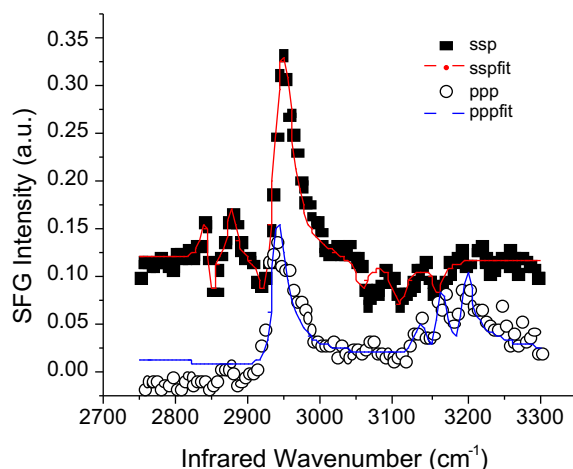
**Figure 1.** Schematic of cell used in SFG study of graphene–ionic liquid interface. Cell is made of glass and evacuated to  $<5 \times 10^{-5}$  Torr pressure. Laser beams enter through the  $\text{CaF}_2$  prism and the graphene and are overlapped at the surface. SF signal exits in reflection through the prism.

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{R}}^{(2)} + \chi_{\text{NR}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma}$$

SFG signal is proportional to the square of the effective susceptibility,  $|\chi_{\text{eff}}^{(2)}|^2$ . Thus the SFG spectra often display the resonant signal as peaks, dips, or derivative shape depending on the relative phase of resonant and non resonant  $\chi^{(2)}$ .

Results of the SFG spectra for the polarization combination (SF, vis, IR) ssp and ppp are displayed in Figure 2. The spectra appear to be dominated by the large resonance at  $\sim 2950 \text{ cm}^{-1}$ , which is assigned to the antisymmetric  $\text{CH}_3$  stretch of the methane sulfate anion [10]. The antisymmetric peak is dominant in both ssp and ppp polarization spectra. Peak fitting analysis gives a ratio for the  $\text{CH}_3(\text{asym})$  ppp/ssp of  $3.7 \pm 0.36$ . The strength of this mode and the lack of strong signal in other vibrational modes in the ionic liquid suggest that this is the species most highly oriented and likely interacting directly with the graphene surface. The peaks are combined with the non resonant background signal of the graphene layer.

The cation also displays several modes although much weaker than the methyl sulfate anion: the  $\text{CH}_3(\text{sym})$  mode ( $2875 \text{ cm}^{-1}$ ) and dips at  $2855$  and  $2916 \text{ cm}^{-1}$  that are due to the  $\text{CH}_2$  (sym) stretch and Fermi resonance, respectively [13–15]. More cation peaks are observed at  $3060$ ,  $3105$ , and  $3165 \text{ cm}^{-1}$ , which are due to the aromatic imidazolium ring. These assignments are likely



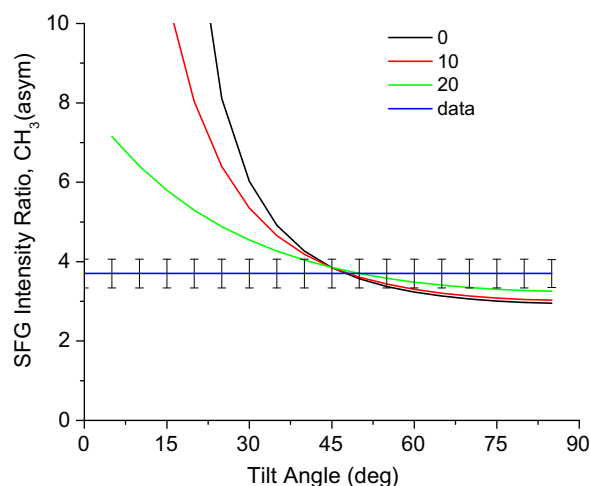
**Figure 2.** SFG polarization spectra for [BMIM][MS] on graphene. Intensities are uncorrected. ■ – ssp polarizations, ○ – ppp polarizations (offset by  $-0.05$ ). Lines are a curve fit to equation.

due to the C–H stretch at the C2 ring position, and the H–C4–C5–H antisymmetric and symmetric stretch combinations.

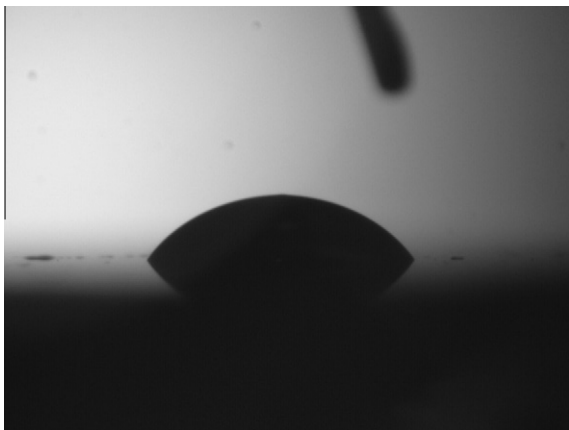
The intensity of the various peaks in the polarization SFG spectra can be used to estimate the average orientation of functional groups at the solid–liquid interface [12,16–20]. The peaks due to the imidazolium cation are too weak for quantitative analysis, however the results suggest that the butyl chain is oriented mostly along the surface plane of the graphene. This assessment is based on the weak signal of the  $\text{CH}_3$  modes and the presence of the  $\text{CH}_2$  peaks. Extension of alkyl chains along the graphite surface has been observed by others [21,22]. Further, in many SFG spectra of ionic liquids, the spectra are dominated by the terminal methyl groups of the butyl chain, especially at non-polar interfaces [7]. In addition, the orientation of the aromatic cation ring is typically orientated parallel to the surface plane at a non-polar interface. However, the appearance of the C–H stretching modes from the aromatic ring indicates that the imidazolium is tilted somewhat out of the interface plane. The orientation of the imidazolium ring is more indicative of its arrangement at a polar interface [6,7]. Previous SFG studies of ionic liquids on non polar interfaces, such as alkylsilane monolayers on quartz, [7] display a high degree of orientation from the alkane chain of the ionic liquid cation. This was explained as due to the favorable dispersion force interaction of counter oriented methyl groups between the monolayer and the alkyimidazolium. The greater polarizability of the aromatic graphene, in contrast to the methyl groups of alkylsilane, influences the strength of the charge interactions with the surface as well.

The SFG signal of the methane sulfate anion also provides some indication the ionic liquid is interacting with a polar interface. The SFG spectra are dominated by the  $\text{CH}_3(\text{asym})$  peak of methane sulfate. The large intensity suggests that the anion is more strongly interacting with the surface providing a higher degree of orientation leading to the greater signal. Anion adsorption from the ionic liquid has been observed for other polar solid–liquid interfaces such as  $\text{TiO}_2$ , quartz, and salts [23,24]. This results is somewhat surprising for graphene due to its non-polar nature. However, this observation implies that the substrate might influence the surface properties of the graphene, making it different than those of graphite.

The orientational angle of the methyl group is estimated by the ratio of  $\text{CH}_3(\text{asym})$  in ppp/ssp spectra. The graph in Figure 3 displays the dependence of this ratio on the tilt angle from the surface



**Figure 3.** Plot of SFG intensity ratio of  $\text{CH}_3(\text{asym})$  in ppp/ssp polarization vs. the tilt angle of the C3 axis of the methyl group on methyl sulfate. Each curve represents a GAUSSIAN distribution width from  $0^\circ$  (delta function) to  $20^\circ$ . The solid horizontal line at 3.7 is the experimental value.



**Figure 4.** Sessile drop of [BMIM][MS] on graphene monolayer on CaF<sub>2</sub> substrate.

normal of the C3 axis. Each curve represents a different GAUSSIAN distribution width to the average tilt angle. Also shown in Figure 3 is the experimental ratio as a horizontal line. The experimental line intersects the theoretical results at tilt angles greater than 40° from the surface normal. This result is consistent with the methyl sulfate tilted from the surface normal at a relatively large angle and adopting a wide range of orientations.

The interaction of [BMIM][MS] with graphene is also characterized as relatively strong by the low contact angle that has been measured, Figure 4. The contact angle is  $58 \pm 2^\circ$ , and indicates the graphene is wet by the ionic liquid. This is slightly lower than water contact angle on graphene,  $\sim 90^\circ$  [25]. This might be due to the SiC substrate, used in those studies or the preparation conditions.

The SFG results on the surface interaction between graphene and the ionic liquid are consistent with other results of ionic liquids with graphite. Atkin and Warr [26] investigated the ionic liquid–graphite–Si<sub>3</sub>N<sub>4</sub> interface with atomic force microscopy. Their results also suggest an interaction of the ionic liquid with the surface that is relatively weak, compared to mica, and mostly due to the alkyl chains of ethyl ammonium nitrate and propyl ammonium nitrate. When the ionic liquid 1-ethyl-3-methylimidazolium acetate was used the force curves suggested a ring oriented somewhat parallel to the graphite plane and alkyl chain extended along the surface with a few layers extended between the tip and graphite surface.

Recent molecular dynamic (MD) simulations also show that the [BMIM][PF<sub>6</sub>] ionic liquid interacts and orients at the graphene surface [3]. The simulations show that the anion and cation both are orientated at the surface and the imidazolium ring is slightly tilted to the surface plane with the alkyl chain extended parallel to the surface plane. The results also show that there is some charge transfer to the ionic liquid and thus a perturbation in the vibrational spectrum is possible, a small shift in the vibrational peaks is observed in the SFG spectra. Similarly the MD simulations show low binding energies to the graphene and essentially Van der Waal type interaction. In these simulation the only a single layer of

graphene in vacuum is considered, however the substrate might influence the graphene surface properties. In fact, due to difference in chemical potential, charge transfer occurs at the interface between graphene and its substrates or adsorbed molecules, which have been utilized to dope graphene or make graphene-based chemical sensors [27,28].

The SFG results indicate that the ionic liquid [BMIM][MS] interacts with the graphene surface and that the both cation and anion are arranged at the surface. The anion appears to be bound to the surface with the methyl group oriented at tilt angle of  $>40^\circ$ . The cation is arranged with the imidazolium ring slightly tilted from the surface plane and the alkyl chain extended along the surface. For the ionic liquid on graphene, the SFG observation is that the ions are not strongly adsorbed or highly oriented, but the contact angle shows a high degree of interaction through wetting. Thus the two measures are not complimentary.

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