Influence of Water on the Orientation of Cations at the Surface of a Room-Temperature Ionic Liquid: A Sum Frequency Generation Vibrational Spectroscopic Study

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Sum frequency generation vibrational spectroscopy was used to determine the orientation of the cations in a room-temperature ionic liquid at the air−liquid interface. The ionic liquid that was studied was 1-butyl-3-methylimidazolium bis-trifluoromethylsulfonimide, [BMIM]$^+$[imide]$^-$. The orientation of the cation, [BMIM]$^+$, was studied as a function of water pressure in the vapor over the range of 10^{-5} to 200 Torr. At water pressures below 10^{-4} Torr, the imidazolium ring was oriented parallel to the surface plane. On increasing the water pressure to greater than 10^{-4} Torr, the imidazolium ring tipped up from the surface with an angle along the surface normal of 40−55°. No water signal was observed in the spectra obtained at the water pressures studied here.

Introduction

Ionic liquids are becoming a major research topic because of their unique physical and chemical properties. Ionic liquids are a combination of organic cations and inorganic anions that are liquid at room temperature. They are useful as a liquid phase in biphasic catalysis and as a medium in liquid/liquid extraction.[1−3] Furthermore, their ionic nature makes them suitable for use as conductive media in batteries, fuel cells, and solar cells.[4−6] Because many of these applications involve interfacial chemistry, it is important to identify the structure of the ions at the interface to develop a molecular-level understanding of their properties.[7,8] The effect of water on the properties of ionic liquids is also of interest because despite its limited solubility in these liquids water greatly reduces their utility in many applications.[9,10] In the present study, we used surface vibrational spectroscopy to investigate the properties of a common room-temperature ionic liquid at the gas−liquid interface. The insights gained in this work give a better understanding of the surface chemistry of ionic liquids.

The ionic liquid that was chosen for study was 1-butyl-3-methylimidazolium bis-(trifluoromethyl sulfon)imide ([BMIM]$^+$-[imide]$^-$). The surface vibrational spectrum of this ionic liquid was recorded using sum frequency generation (SFG) spectroscopy. We used this type of spectroscopy to probe the changes that occur to the cation in [BMIM]$^+$[imide]$^-$ at the gas−liquid interface as the pressure of water in the vapor (P_{H_2O}) was varied from 10^{-5} to 10^2 Torr. The results suggest that at P_{H_2O} < 5 × 10^{-4} Torr the imidazolium ring is parallel to the plane of the surface and the butyl chain is extended into the vapor phase. As the water pressure increases, the change in the SFG signal of the imidazolium ring is consistent with a reorientation of the ring to a tilt orientation of 40−55° from the surface normal and a twist orientation of 0−45° about the ring's psuedo-C_2 axis. The maximum signal from the imidazolium ring occurs at $P_{H_2O} \approx 1$ Torr. The water signal was not observed at any of the pressures studied here.

Nonlinear Spectroscopy. SFG is a nonlinear spectroscopic technique that selectively probes molecules at an interface that has preferential polar ordering. SFG does not detect isotropically oriented molecules. The applications and theory behind surface SFG have been discussed in numerous reviews.[11−16] The SFG experiment involves overlapping two laser beams (one in the infrared and one in the visible region) on the surface of the liquid to generate a third beam at the sum of the two incident beams. When the frequency of the infrared beam matches a resonance of the surface molecule, the SFG process is enhanced. A plot of sum frequency intensity versus wavenumber is interpreted as a vibrational spectrum of the surface molecules. Varying the input polarizations and analyzing the output polarizations provides information on the molecular orientation.

Intensity in an SFG spectrum is proportional to the square of the induced polarization, $P^{(2)}$:

$$I_{SF} = |P^{(2)} = \chi^{(2)}:E_{vis}E_{IR}|^2 \tag{1}$$

E is the electric field of the incoming visible and infrared light fields, and $\chi^{(2)}$ is the second-order nonlinear susceptibility tensor. The measured $\chi^{(2)}$ is modified by the magnitude of the local fields at the surface, which are generally determined by use of Fresnel's equations. The susceptibility contains all of the information on the molecule related to SFG spectroscopy through the hyperpolarizability, $\beta^{(2)}$.

$$\chi^{(2)}_{res} = \frac{N\langle\beta^{(2)}\rangle}{(\omega_{IR} - \omega_q + i\Gamma_q)} \tag{2}$$

The brackets, ⟨ ⟩, indicate an orientational average over the Euler angles, and N is the number of modes contributing to the signal. The denominator in eq 2 describes the resonance condition for the susceptibility, where ω_q is the frequency of the normal mode, ω_{IR} is the input infrared frequency, and Γ_q is the damping constant for the qth vibrational mode. The hyperpolarizability is related to the molecular properties by the product of the Raman polarizability, α, and the infrared transition dipole, μ, as follows:

$$\beta^{(2)}_{abc} = \langle g|\alpha_{ab}|v\rangle\langle v|\mu_c|g\rangle \tag{3}$$

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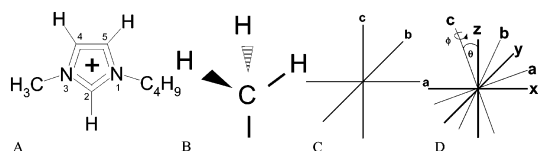*J. Phys. Chem. B, Vol. 107, No. 25, 2003* **6149**

Figure 1. (A) 1-Butyl-3-methylimidazolium cation with a numbering system, (B) the methyl group, (C) definition of the imidazolium ring-centered and carbon-centered coordinate system (*abc*), (D) mutual orientation of the (*abc*) coordinate system with respect to the surface frame (*xyz*) with tilt angle, θ, and twist angle, ϕ.

Here, *abc* refers to the Cartesian coordinates centered on the molecule or functional group. To relate the quantities measured in the laboratory reference frame to the molecular properties described in a molecule-based coordinate system, the specific dipole and polarizability elements are transformed using rotational matrices.

Experimental Section

Optical System. The laser used in these experiments was a picosecond pulsed Nd:YAG (Ekspla) pumping an optical parametric generator/amplifier OPG/OPA (LaserVision) to generate infrared light tunable between 1000 and 4000 cm^{-1}. The infrared beam has an energy of 300 μJ at 3000 cm^{-1} and a bandwidth of $\sim$7 cm^{-1}. A visible beam (532 nm) is created by second-harmonic generation in a KTP crystal. The angles of incidence at the surface of the infrared and visible beams were 60 and 50°, respectively, with an energy density of $\sim$10 mJ/cm^2.

The SFG setup was controlled using the program LabVIEW, which scans the infrared frequency and collects the signals from the gated integrator. Data presented here are an average of five scans each of 20 shots/point, continuously scanned at 1 cm^{-1}/s. All data were corrected for fluctuations in the infrared and visible light by simultaneously collecting the SFG signal generated in a *z*-cut quartz reference sample. Spectra recorded at the same partial pressure of water are intensity normalized to the CH$_3$(sym) signal in the *ssp* spectrum (*ssp* = s_{SF}, s_{vis}, and p_{IR} are the polarizations of the optical beams).

Sample Preparation. The ionic liquid 1-butyl-3-methyl-imidazolium bis-(trifluoromethylsulfon)imide was donated by Professor Kenneth Seddon of The Queen's University. The sample was filtered through a 10-μm frit and placed in a glass cell with Teflon/Kalrez O-rings and stopcocks.

The procedure used to prepare the samples for the spectroscopic measurements was similar to that of Brennecke et al.[17] Briefly, prior to conducting each experiment at room temperature, the sample was evacuated to $\sim$10^{-5} Torr on a N$_2$(l) trapped glass vacuum line with nongreased joints and then heated to 90 °C in the cell for several hours. Water purified by a Millipore A10 water system has a resistivity of 18 MΩ·cm and a total organic content of less than 7 ppb (determined by a TOC meter). Water was introduced into the sample by exposing the sample to water vapor at the desired pressure for at least 2 h before the spectrum was recorded. Pressure was measured using an ionization gauge or a manometer, and temperature was monitored with a type-K thermocouple.

Results

The numbering scheme for the imidazolium ring is shown in Figure 1. The polarization data for [BMIM]$^+$[imide]$^-$ at 10^{-5} Torr H$_2$O and 1 Torr H$_2$O are presented in Figure 2. The spectra contain six resonances (Table 1). The peaks at 2850 and 2875 cm^{-1} are due to the symmetric stretch of the CH$_2$ and CH$_3$ alkyl

TABLE 1: Peak Positions and Spectroscopic Assignments[a]

peak	assignment	position (cm^{-1})
1	CH$_2$(sym)	2850
2	CH$_3$(sym)	2880
3	CH$_3$(FR)	2840
4	CH$_3$(asym)	2960, 2980
5	H$-$C(4)C(5)$-$H(asym)	3120
6	H$-$C(4)C(5)$-$H(sym)	3175

peak	ssp		ppp		sps	
$P_{H_2O} \rightarrow$	10^{-5}	1	10^{-5}	1	10^{-5}	1
1	2.30	0.80				
2	6.70	6.40				
3	4.70	4.20				
4	4.35	3.80	4.20	5.30	1.40	1.35
5		1.50		1.00	0.05	0.05
6		1.95		0.90	0.40	0.65

[a] Values indicate relative peak amplitude under the indicated SFG polarization combination and water pressure.

groups, respectively. The peaks at 2935 and 2945 cm^{-1} are the Fermi resonances of the CH$_3$ bending overtone and the antisymmetric CH$_3$ stretch, respectively.[18,19] Finally, the peaks in the aromatic ring C$-$H region at $\sim$3120 and 3170 cm^{-1} are due to the antisymmetric and symmetric H$-$C(4)C(5)$-$H stretches, respectively.[20,21]

The *ppp* polarization spectrum contains a peak at 2970 cm^{-1} that is assigned to the antisymmetric CH$_3$ stretching vibration, along with weak features in the range of 3100$-$3200 cm^{-1} assigned to the C$-$H modes of C(4) and C(5). The *sps* spectrum contains a peak at $\sim$2980 cm^{-1} that is due to the antisymmetric CH$_3$ stretching vibration as well as a small peak at 3170 cm^{-1} that is assigned to the symmetric H$-$C(4) C(5)$-$H stretch.

The peaks observed in the spectra appear to be only from the aromatic ring or the butyl chain. Neither the CH$_3$(sym) stretch on the nitrogen (N3), expected at $\sim$2930 cm^{-1},[21,22] nor the C$-$H stretch at the C(2) carbon that would be expected at $\sim$3000 cm^{-1} is observed. In addition, none of the features in these SFG spectra is characteristic of water (3200$-$3750 cm^{-1}).

Discussion

Orientation Analysis. A diagram of the imidazolium ion and the ring-fixed coordinate system is given in Figure 1. The imidazolium ring lies in the *a*$-$*c* plane. The orientation of this ring is defined in terms of the tilt angle (θ) of the *c* axis with respect to the surface normal (*z* axis) and a twist angle (ϕ) corresponding to the rotation of the ring about the ring-fixed *c* axis. A tilt of 90° and a twist of 90° would bring the ring parallel to the surface plane.

The orientation of the cation (methyl group and ring) is established on the basis of the polarization dependence of the SFG spectra following the procedure of Hirose et al.[23$-$25] This model assumes that the methyl group can freely rotate around the C$-$C axis and that the local symmetry is C_{3v}. The H$-$C(4)C(5)$-$H group is treated as having local C_{2v} symmetry.[21] To make use of the relations between orientations and $\chi^{(2)}$, the magnitudes of the tensor elements in the Raman polarizability and dipole vectors must be known. These were determined from the single-bond dipole and polarizabilities; their values are presented in Table 2. The procedure for converting the single-bond values into normal-mode values is provided in the references cited in Table 2.

The susceptibility is a third-rank tensor with 27 elements; however, for a liquid surface, this reduces to only three independent elements, χ_{yyz}, χ_{zzz}, and χ_{xzx} ($= \chi_{zxx}$). The values
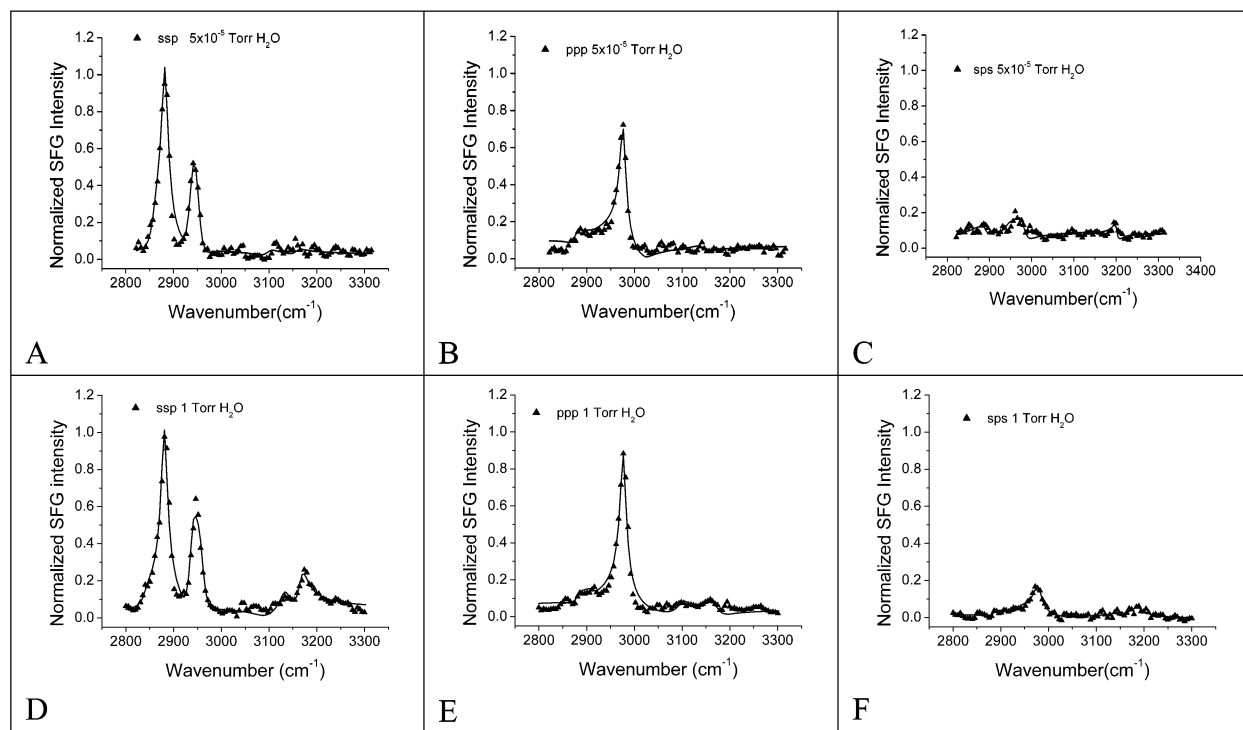
Figure 2. SFG spectra of [BMIM]$^+$[imide]$^-$ at the air–liquid interface. (A) *ssp* polarization, (B) *ppp* polarization, and (C) *sps* polarization. A–C were recorded at a water pressure of 5×10^{-5} Torr H$_2$O. (D) ssp polarization, (E) *ppp* polarization, and (F) *sps* polarization. D–F were recorded at 1 Torr of H$_2$O. Lines are a fit to eq 2.
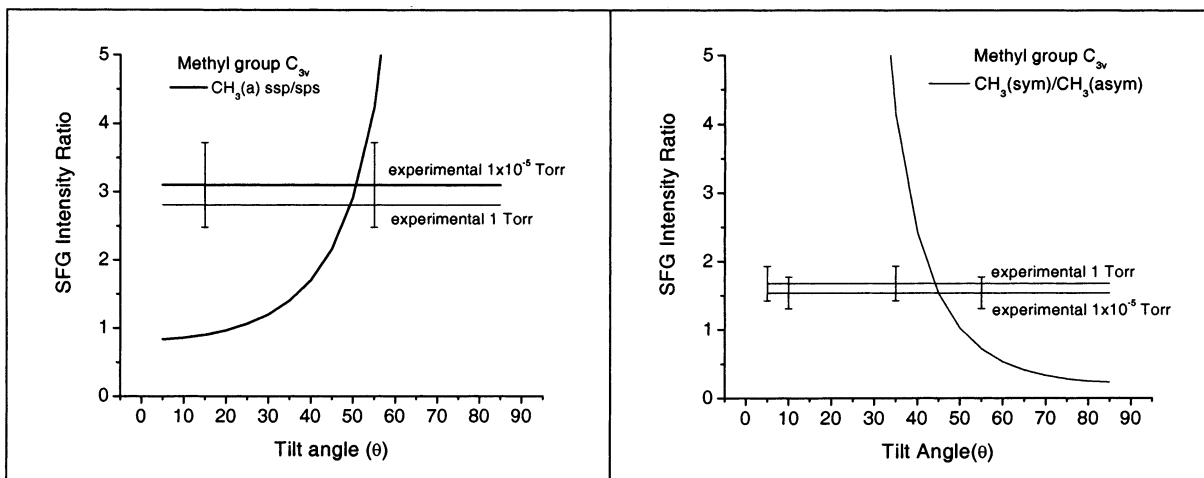

Figure 3. Simulation of the influence of various tilt angles on the orientation of the CH$_3$ on the butyl group in [BMIM]$^+$. Model assumes free rotation around the C3 axis. Experimental measured results are present as horizontal lines with error bar at 1 standard deviation.

TABLE 2: Bond Dipole and Polarizability Used in Orientation Analysis

vibration	dipole	polarizability[39–41]
CH$_3$	0.6 [18,19,42]	1.44
H–CC–H	1.057 [43]	1.147

are deduced by analyzing the output polarizations that result from different combinations of input polarizations. For example, *ssp* (*s*-SF, *s*-vis, and *p*-IR) polarizations will probe the χ_{yyz} tensor element. In this paper, the ratios of various SFG intensities are simulated as a function of tilt (θ) and twist angles (ϕ) for the imidazolium cation (Figure 1c). These simulated values are then compared to the measured intensity ratios to determine the tilt and twist angles that are consistent with the experimentally determined SFG spectra. Figures 3 and 4 present the results of the simulations of the CH$_3$ and H–C(4)C(5)–H groups in

[BMIM]$^+$, respectively. The ratio of the SFG intensities is presented as a solid horizontal line, and the intersection of the line with the theoretical curve provides the range of values over which the tilt–twist angles are consistent with the data. This analysis assumes a delta-function angle distribution and an isotropic $x-y$ surface plane.

Neat Liquid. At pressures of less than $\sim10^{-4}$ Torr, the only peaks observed in the SFG spectra are those of the methyl group at the end of the butyl chain (Figure 2). Given that SFG is sensitive only to groups at the surface, this suggests that the butyl chains are protruding out of the surface into the vapor phase. This result is consistent with the theory that surface composition is dominated by the lowest-energy component of the system, which in the present experiments is the alkyl chain on the imidazolium ring. In this system, the cation is likely to be the dominant species at the surface because it is the most
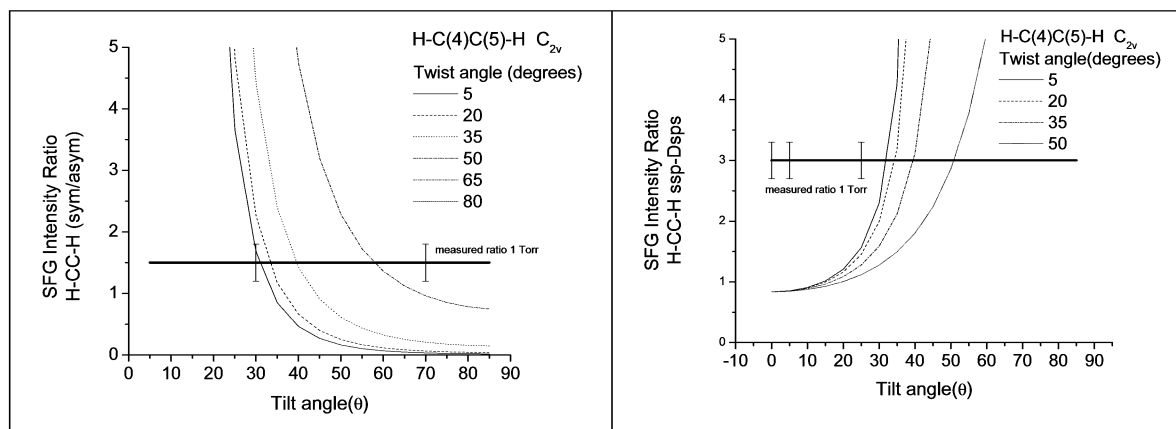
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Figure 4. Simulation of the influence of various tilt−twist angles on the orientation of the H−C(4)C(5)−H group in [BMIM]$^+$.
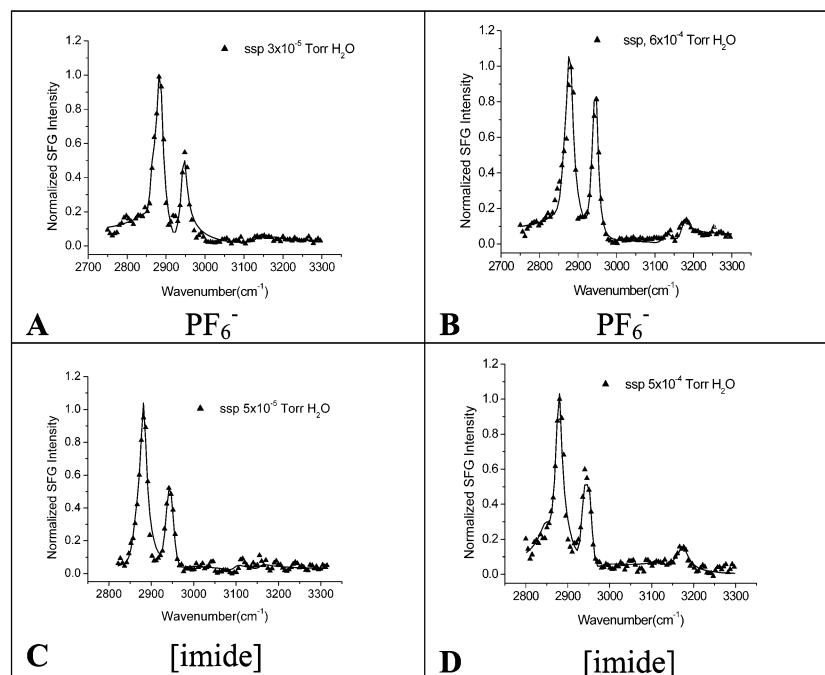

Figure 5. (A) 10^{-5} Torr [BMIM$^+$][PF$_6^-$], (B) 10^{-4} Torr [BMIM$^+$][PF$_6^-$], (C) 10^{-5} Torr [BMIM$^+$][imide$^-$], and (D) 10^{-4} Torr [BMIM$^+$][imide$^-$]. Pressures indicate the partial pressure of water. Lines are a fit to eq 2.

polarizable species (because of charge delocalization) in the imidazolium ring. It is believed that the alkyl chain is directed into the vapor to keep the charged imidazolium ring close to the anion. Furthermore, the SFG results suggest that the imidazolium ring lies parallel to the surface. Given that SFG predominantly probes vibrations with polar ordering (modes with a dynamic dipole projection along the surface normal), the tendency of the imidazolium ring to lie parallel to the surface plane will cause the dipole projections of the ring C−H vibrations to be mostly aligned along the surface. Thus, C−H ring vibrations do not appear in the *ssp* or *ppp* spectrum. If the imidazolium ring is parallel to the surface normal, then the antisymmetric or symmetric modes of the H−C(4)C(5)−H vibration or the C(2)−H vibration should be observed; however, they are not seen for the neat liquid.

At water pressures greater than 5×10^{-4} Torr, peaks corresponding to those of the imidazolium ring are detected (Figure 2D); specifically, the H−C(4)C(5)−H symmetric stretch at ∼3175 cm^{-1} and the antisymmetric stretch at ∼3130 cm^{-1} are observed. The appearance of both the symmetric and antisymmetric modes indicates that the ring tilts to project the C(4) and C(5) carbons along the surface normal, and the

appearance of the antisymmetric stretch suggests that the ring twists about its psuedo-C_2 axis. The SFG intensity is found to be consistent with a tilt of 40−55° and twist of 0−45° at the surface.

The methyl groups on the butyl chain change their orientation at the surface when the water pressure is increased to pressures greater than 5×10^{-4} Torr. However, the methyl groups on the butyl chain are less sensitive to this change, presumably because of the flexibility in the chain. The methyl group orientation changes from a tilt angle of 30−45° to 35−60° with the addition of water. Both results suggest the methyl group has free twist rotation about the C−C bond (Figure 3).

In the bulk phase, the anions in the ionic liquid tend to be coordinated or hydrogen bonded to the aromatic protons of the imidazolium ring (i.e., in the plane of the ring).[26−28] However, results have also been obtained that support the coordination of the anion to the cationic ring (i.e., above or below the ring), an arrangement in which the association between ions is dominated by Coulombic interactions.[29−32] The relative orientation of the ions at the surface may differ from that in the bulk because the 3D symmetry of the interactions is broken at the interface. Surface tension results for ionic liquids are consistent

with ion pairs in close contact, as in concentrated H_2SO_4.[33] These surface tension results, obtained by Watson's group, support the presence of alkyl chains at the surface.[34]

The addition of water to an ionic liquid influences the solvation of the ions in the liquid and consequently affects their orientation with respect to each other. Studies of bulk ionic liquids containing water indicate only a relatively weak interaction between the water molecules and the ions.[10] For example, infrared spectroscopic data indicates that water exists mostly as monomers in mixtures of water with $[BMIM]^+$ and certain anions.[10] In the present work, the intensity of the H−C(4)C(5)−H signal is greater for the imide than in the $[PF_6{}^-]$ system and is possibly related to the strength of the hydrogen bond with the anions, where the strength is less for $[PF_6{}^-]$ than for the imide. The solubility of water in $[PF_6{}^-]$ and the imide is similar.[10] The weak hydrogen bonding of water with ions in solution appears to be sufficient to cause a reorientation of the cation and results in a tilting of the aromatic ring. Furthermore, hydrogen bonding between water and the C(2) hydrogen may account for the ring tipping so as to point this group into the bulk liquid.[27] Fluorescence studies suggest that ionic liquids are moderately polar compounds, further supporting the weak bonding of water in the liquid.[35,36] Reevacuation of the sample to 10^{-5} Torr caused the ring modes to disappear, indicating that the influence of water is completely reversible. Water features are not observed in the spectra, possibly because it does not adopt a polar-oriented orientation at the interface.

SFG Model of the Surface in Relation to Ion-Scattering Results. At low water concentration, the features of the SFG spectra are consistent with an interfacial structure in which the butyl chains extend into the gas phase, away from the surface, and the imidazolium rings lie parallel to the surface. At higher water concentrations, the rings tip along the surface normal, the butyl chains remain extended into the vapor phase, and the C(2) carbon is directed toward the bulk liquid. This structure is different from that proposed by Watson's group on the basis of ion scattering experiments.[37,38] In their model, the plane of the ring is parallel to the surface normal with the C(2) carbon directed toward the vapor and the alkyl chain mostly along the surface. However, if this orientation was present, then we would expect a strong signal at 3030 cm^{-1} at all pressures, and no such signal is observed. SFG experiments conducted using $[PF_6{}^-]$ as the anion also indicate that the ring is tipped along the surface normal at water pressures greater than 1×10^{-4} Torr, as with the imide anion (Figure 5). Future experiments using a wider variety of anions and theoretical calculations will help to resolve these differences in surface orientation determined by SFG and ion scattering.

Conclusions

SFG spectroscopy was used to determine the orientation of the cations at the surface of a room-temperature ionic liquid. The results suggest that at water pressures less than 10^{-5} Torr the imidazolium cations are oriented such that their ring lies parallel to the surface, and at higher water concentrations, their ring is tipped along the surface normal.

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