Sum Frequency Generation Spectroscopy of Dicyanamide Based Room-Temperature Ionic Liquids. Orientation of the Cation and the Anion at the Gas−liquid Interface

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The orientation of the cation and the anion of room-temperature ionic liquids using sum frequency generation vibrational spectroscopy is reported. The ionic liquids are based on butyl-methyl imidazolium $[BMIM]^+$ and hexyl-tributyl ammonium $[N6444]^+$ together with dicyanamide $[DCA]^-$ as the anion. The tilt angle of the C_3 axis of the methyl group from the alkyl chain in the cations was found to vary from 52° to 80° as a function of the distribution width σ (which ranges from 0° to 30° with respect to the surface normal) for [BMIM]-[DCA] and similarly for [N6444][DCA]. The orientation of the C_2 axis in the dicyanamide anion as a function of the twist angle ϕ, varied between 46° and 90° for [BMIM][DCA] and from 53° to 90° for [N6444][DCA]. These results suggest the presence of both ionic species at the gas−liquid interface and help describe the behavior of a simple inorganic anion at the surface.

1. Introduction

Composed in their entirety of ions, room-temperature ionic liquids (RTILs) are salts that have received an abundance of attention in the past few years. They are liquid at room-temperature because of weak interactions between the charged species, and they are usually formed by an asymmetrical organic cation and a poorly coordinating anion, which can either be organic or inorganic.[1−3] These compounds show, high conductivity, low volatility, wide electrochemical windows, thermal stability, and are liquid for wide temperature ranges.[2,4−9] The RTILs are also good solvents for a large variety of organic and inorganic compounds.[5,7,10]

The applications of ionic liquids are many. They have emerged as green solvents with potential in liquid−liquid extraction, synthesis, catalysis, and biocatalysis, as electrolytes in fuel cells and batteries, as supporting media for homogeneous and heterogeneous catalysis, and as part of the composition of new materials.[11−15] Their unique properties make them also suitable for flue gas scrubbing operations for pollutants such as SO_2.[16,17] They have also been proposed for use in supercritical extraction operations because of the relatively high solubility of CO_2 in those compounds.[18,19] Since their high viscosity limits the possible industrial applications, attention has been focused lately on compounds with anions that can form RTILs with lower viscosity.[9] This is because the anion is usually responsible for dictating several of the physical properties of an ionic liquid.[7] Therefore, the properties of some compounds based on anions such as triflate, bis(trifluoromethanesulfonyl)imide, and dicyanamide (DCA^-) have been investigated.[4,9,20−23] Various DCA^- based RTILs have low melting points, can be synthesized at relatively low costs, and possess low viscosities as well as donor solvent characteristics.[9,24] Moreover, the dicyanamide ion is an anionic bridging ligand that has Lewis base attributes, which creates the opportunity to synthesize ionic liquids with very specific properties[5,21] Therefore, knowledge about the structure of the species at the interface is of great interest because of its the ubiquitous role in mass transfer operations such as gas accommodation and heterogeneous catalytic reactions. In addition, the interest resides in gaining fundamental knowledge about the surface structure and surface energy.

This work reports sum frequency generation spectroscopic studies of the gas−liquid interface of two room-temperature ionic liquids: 1-butyl-3-methyl-imidazolium dicyanamide [BMIM]-[DCA] and hexyl-tributyl-ammonium dicyanamide [N6444]-[DCA]. These two compounds possess vibrational modes in the range of the C−H (2750−3300 cm^{-1}), and C≡N (2000−2300 cm^{-1}) vibrations. Previous studies conducted in this research group focused mainly on the investigation of the surface of RTILs containing anions whose vibrational frequencies are not easily detectable with the sum frequency spectroscopy set up in use, such as $[BMIM][PF_6]$, and $[BMIM][BF_4]$.[25,26] The most accessible and widely used frequency range for SFG experiments, lies in the range of 1500−4000 cm^{-1}, which includes the vibrational frequencies of C−H, C≡N, C=O, and O−H stretches, among others.

The advantage of working with RTILs formed by cations and anions that possess functional groups susceptible of being probed by a vibrational technique with a convenient wavelength range is that it makes it possible to gain insight on the structure at the interface and to develop a more complete description of it, since both ionic species are detected. In addition, dicyanamide is an important ion to study because of its inorganic nature, as most ionic liquid-forming inorganic anions do not generate SFG signal (halides), and others, such as BF_4^-, and PF_6^-, besides having a nearly spherical shape, are more centrosymmetric, which would result in lower SFG signal. Moreover, they possess vibrational modes whose frequency cannot be detected because of the experimental constraints of the spectrometer used for these studies which were stated above. In addition, by probing an ionic liquid with an inorganic anion, the results shall be more general to the broader class of ionic liquids that are usually formed by an organic cation and an inorganic anion.

1.1. Sum Frequency Generation (SFG). SFG is a second order nonlinear spectroscopy, sensitive to molecules in non-centrosymmetric environments. In the bulk of a liquid there is inversion symmetry, which forbids the generation of sum

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frequency signal. However, at the surface that symmetry is broken and SFG is allowed. In this technique, two high-intensity laser beams of frequencies ω_1 and ω_2, overlap at the surface of a nonlinear medium and generate a second order nonlinear polarization $P^{(2)}_{(\omega_1+\omega_2)}$ to which the intensity of the sum frequency signal is proportional.

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

Where E_{VIS} and E_{IR} are the electric fields of the incoming visible and infrared beams respectively, and $\chi^{(2)}$ is the second order nonlinear susceptibility. The susceptibility has a non-resonant χ_{nr} and a resonant contribution $\chi_{res}^{(2)}$:

$$\chi^{(2)} = \chi^{(2)}_{res} + \chi^{(2)}_{nr} \tag{2}$$

$\chi^{(2)}_{nr}$ is a background contribution from the interface and $\chi_{res}^{(2)}$ includes contributions from individual resonant modes and contains the molecular hyperpolarizability $\beta^{(2)}$. This is written as follows:

$$\chi^{(2)}_{res} = \sum \left(\frac{N\langle\beta^{(2)}\rangle}{\omega_{IR} - \omega_q + i\,\Gamma_q} \right) \tag{3}$$

Where $\langle\beta^{(2)}\rangle$ is the molecular hyperpolarizability averaged over all possible molecular orientations, N is the number of molecules that contribute to the sum frequency generation, Γ_q is the damping constant for the qth vibrational mode, ω_q is the molecule normal mode of vibration, and ω_{IR} is the frequency of the incoming IR beam. The intensity of the SFG signal (I_{SF}) is proportional to the square of the absolute value of the nonlinear polarization. It is then evident that whenever ω_q becomes comparable to ω_{IR}, the intensity of the signal is enhanced, resulting in a peak in the spectrum.[27-29]

2. Experimental Section

2.1. Materials. We purchased 1-chlorobutane 99%, 1-methylimidazole redistilled 99+%, ethyl acetate anhydrous 99.8%, 1-iodohexane 98+%, tributylamine 98.5+%, silver nitrate >99%, and hexane 98.5% ACS reagent were from Aldrich, sodium dicyanamide 96% was obtained from Alfa Aesar, and all were used as received. The water is deionized using a Millipore A10 system and has a resistivity of 18 MΩ-cm and a TOC index of <3 ppb.

2.2. Samples. The ionic liquids used in this study, [BMIM]-[DCA] and [N6444][DCA], were synthesized according to literature methods.[5,9,30,31] For [BMIM][DCA], the cation was synthesized by mixing 1-methylimidazole with 1-chlorobutane in a 1:1.1 molar ratio and the mixture refluxed under inert gas at a temperature of 65 °C for 72 h. The resulting 1-butyl-3-methyl-imidazolium chloride ([BMIM][Cl]) was then washed three times with ethyl acetate and then dried under vacuum to a pressure of 5×10^{-5} Torr.

[N6444]$^+$ was prepared by mixing tributylamine and 1-iodohexane in a 1:0.85 molar ratio, in acetonitrile. The mixture was then refluxed under nitrogen at 70 °C for 5 days. Hexane was added to the resulting solid mass while still hot and the mixture was stirred to obtain a very brittle solid upon cooling, thus facilitating its transfer and washing. The solid was washed with hexane several times and filtered.

The procedure of incorporation of the anion is identical for both cations and was described previously.[32] Silver dicyanamide is added to a suspension of the cation [N6444]$^+$ or to a solution in water [BMIM]$^+$, and the mixture is stirred for 3 h. The
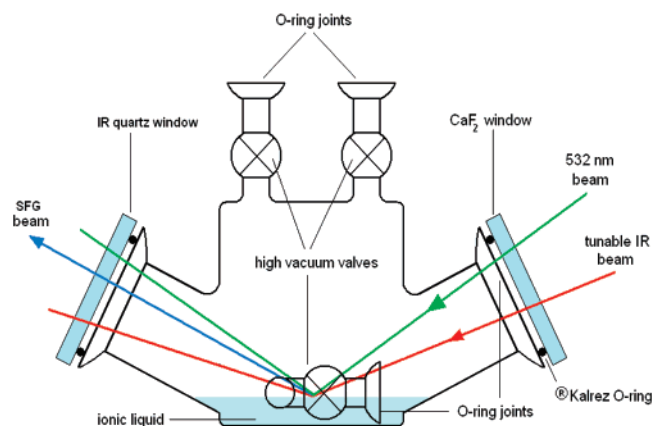

Figure 1. Schematic of the Pyrex SFG cell used in the studies.

precipitate (AgI) is removed and the sample purified, and it was finally dried on a vacuum line to a pressure of 5×10^{-5} Torr.

2.3. Spectroscopy System. The spectroscopy set up was described elsewhere.[32] It consists of an EKSPLA PL2143A/20 picosecond pulsed Nd: YAG laser with a 25 ps pulse and a 20 Hz repetition rate, whose 1064 nm output pumps an optical parametric generation/amplification system (Laser Vision OPG/OPA). The fixed visible and the tunable infrared beams are collimated and overlap at the surface of the liquid following a copropagating geometry, with angles (with respect to the surface normal) of 50° for the visible and 60° for the IR. The SFG signal is then sent to a gated integrator and collected in a computer program.

The SFG cell that contains the sample is cylindrical, made of Pyrex, and comprises two arms set at an angle of 55° from the surface normal, through which the incoming beams and the SFG beam travel (Figure 1). IR quartz, or CaF$_2$ windows are attached to O-ring fittings at the end of the arms, sealed using Kalrez O-rings, and fixed with clamps. The bottom of the cell is optically flat to prevent unnecessary scattering of the beams and thus excessive stray light into the detection system. Prior to being introduced in the SFG cell, the sample is filtered using sintered glass to eliminate any suspended solid particles and then introduced in a glass vial equipped with O-ring joints where it is dried in vacuum. Once the sample is inside the SFG cell, the drying process is started until the desired pressure is reached (5×10^{-5} Torr), and it is finally backfilled with dry argon gas under slight overpressure.

2.4. Data Collection and Analysis.. The frequency of the IR laser beam is scanned at a rate of 1 cm^{-1}/sec. Each data point corresponds to 20 averaged laser shots. Five spectra per polarization combination are obtained, and the average is plotted along with error bars. The data are corrected for fluctuations in the infrared beam by dividing the averaged spectrum by data collected using gold as a substrate. The spectra are then fitted using the software Origin 6.0 and eq 3. The parameters that are varied in the fitting are the amplitude and width of the peak, the nonresonant background, and the wavelength The fitting procedure minimizes the standard deviation between the experimental data and the nonlinear fit curve, and is carried out using instrumental setting which, in addition to the error in the fit, takes into consideration the error due to the scattering of the experimental points.

3. Results

To probe both ionic species, two regions of the infrared were chosen for the spectroscopy. The 2000−2300 cm^{-1} interval for

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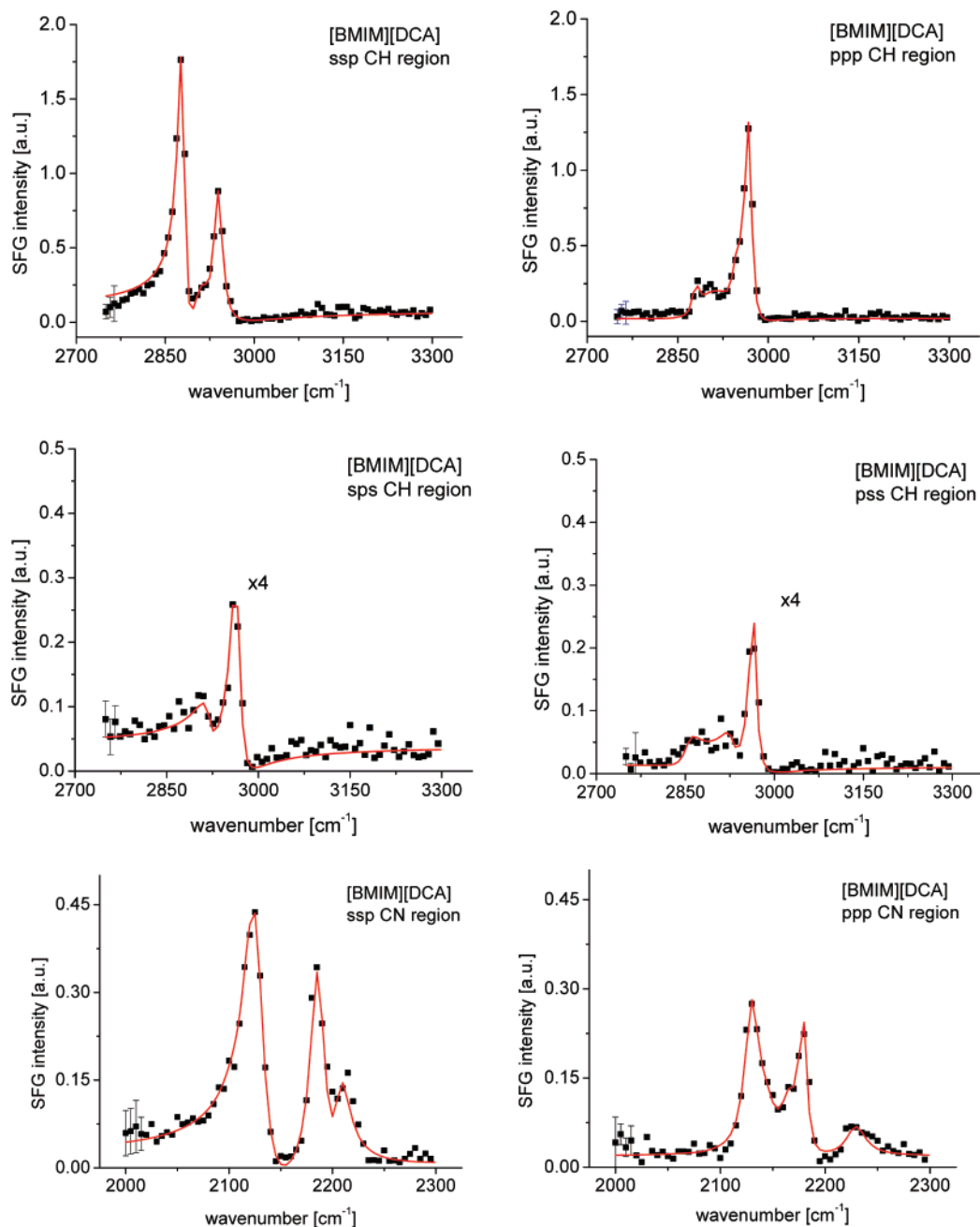*J. Phys. Chem. B, Vol. 111, No. 33, 2007* **9735**

Figure 2. (a) Sum frequency spectra of [BMIM][DCA] at ssp, ppp, sps, and pss polarization combinations for CH stretching region. (b) Sum frequency spectra of [BMIM][DCA] at ssp, and ppp combinations for CN stretching region.

the anion (C≡N stretch vibrational modes) and the 2750−3300 cm^{-1} interval for the cation (C−H stretch vibrational modes).

The spectra for [BMIM][DCA] are shown in Figure 2a and b for polarizations ssp, ppp, sps, and pss for the C−H region and ssp, and ppp for the C≡N region. In the C≡N stretch region, the peaks at ∼2130 cm^{-1} and ∼2180 cm^{-1} correspond to the antisymmetric and the symmetric C≡N stretch, respectively. The peak at ∼2210 cm^{-1} is a combination band of the symmetric and antisymmetric N−C stretching modes.[33,34] Finally, there is an additional peak discernible only in ppp, which seems due to the formation of isonitrile moieties, which were detected in previous IR studies of cyanamide.[35] The polarizations sps and pss are not shown since the amplitude of the peaks is barely above the noise level. The ssp and ppp spectra show a relatively high signal-to-noise ratio, which was found to be characteristic of the dicyanamide anion in other SFG studies of dicyanamide based ionic liquids at the metal−

liquid, and at the titanium dioxide−liquid interfaces.[32,36] In those studies, the signal-to-noise at sps and pss polarizations is also very small. This suggests a lower degree of order of the anion molecules at the surface layer.

The C−H stretching region in the ssp combination contains the symmetric methyl stretch and its Fermi resonance at ∼2879 cm^{-1} and ∼2940 cm^{-1}, respectively.[37–39] The ppp polarization combination contains a peak at ∼2970 cm^{-1}, which corresponds to the antisymmetric methyl stretch.[37,40,41] No aromatic CH ring mode peaks are visible near 3170 cm^{-1}. Also, the methylene group vibrations are weakly present in the spectra, which suggest that the alkyl chains seem to have an all-trans configuration. The sps and pss polarization combinations, although with a lower signal-to-noise ratio, contain the antisymmetric methyl stretch peak at 2960 cm^{-1} as well as a small contribution from the symmetric stretch. The results are summarized in Table 1.

TABLE 1: SFG Vibrational Spectroscopy Results for [BMIM][DCA], and [N6444][DCA][a]

		[BMIM][DCA]				[N6444][DCA]			
		ssp	ppp	sps	pss	ssp	ppp	sps	pss
C−H region	r^+	2877	2879	n/p	n/p	2881	2878	n/p	n/p
	r^+_{FR}	2938	2941	n/p	n/p	2940	s/n	n/p	n/p
	r^-	n/e	2969	2965	2965	n/e	2966	2966	2967
	d^+	2845	s/n	s/n	2855	s/n	s/n	s/n	s/n
	d^-	2920	s/n	2920	2930	2915	2918	2918	2923
C≡N region	as C≡N	2127	2130	s/n	s/n	2122	2126	s/n	s/n
	ss C≡N	2186	2180	s/n	s/n	2184	2188	s/n	s/n
	isonitrile[b]	s/n	2164	s/n	s/n	s/n	2154	s/n	s/n
	ss + as N−C	2207	2219	s/n	s/n	2214	2225	s/n	s/n

[a] s/n, signal-to-noise too low; n/p, not present. [b] According to studies on cyanamide, although this was not fully demonstrated in the present investigation.

The results of this interface are in accordance with other sum frequency spectroscopy results of the ionic liquid−gas interface of imidazolium based compounds, also reinforcing the idea that the anion does not have an influence on the orientation of the cation.[25,26,42]

The spectra of [N6444][DCA] in Figure 3a and b, show the peaks corresponding to the same vibrations as for [BMIM]-[DCA]. Spectra in the C−H stretch region show smaller signal-to-noise compared to the above-mentioned compound, which suggest a lower degree of ordering of the butyl chains. This may be because [N6444]$^+$ has a more spherical shape than [BMIM]$^+$ and it is not possible to discern whether the SFG signal comes from the butyl or hexyl chains, or a combination of all four. Spectra in the C≡N stretch region shows differences in the peak ratios, especially in the case of the antisymmetric stretch:symmetric stretch peak ratio, which is larger compared to the [BMIM][DCA] system in the ssp spectra. There is also an increase in the antisymmetric stretch:combination band peak ratio for [N6444][DCA] in the ppp spectra. Spectra corresponding to sps and pss polarizations in the C≡N region are not shown since the peaks are at the noise level. Similarly to the imidazolium case, this suggests a low degree of ordering of the anion molecules at the gas−liquid interface.

3.1. Orientation Analysis. The orientation of the cation and anion is derived from the principle of polarization dependence of the sum frequency spectra. The procedure is similar to that of Hirose et al.[43−45] and Wang et al.[46,47] The terminal methyl groups of the alkyl chains are assigned C_{3v} symmetry and are considered to possess the freedom to rotate around the C_3 symmetry axis, therefore having an orientation described by the tilt of the axis. The dicyanamide ion is assumed to possess C_{2v} symmetry but no free rotation is assumed around its symmetry axis, and has both a tilt angle, θ, and a twist angle, ϕ.

The principle of polarization dependence compares the ratio of peak intensities of different vibrational modes with theoretical curves of peak intensity ratio versus orientational angle. As stated above, the intensity of the SFG signal (I_{SF}) is proportional to the square of the absolute value of the second order nonlinear susceptibility $\chi^{(2)}$, which in turn is proportional to the hyperpolarizability, $\beta^{(2)}$. The expressions of the hyperpolarizability tensors contain the inverse kinetic energy matrix elements (G matrix elements), which are different for each molecular group. Those elements have been already worked out in the literature for the C−H stretch modes of methine, methylene, and methyl groups.[44,46] However, when molecules with different structures or with atoms other than only carbon and hydrogen are studied, it is necessary to derive new expressions. Therefore, following Wilson's FG matrix method,[48−52] expressions for the kinetic energy matrix elements were obtained for the dicyanamide molecule [DCA]$^-$, where simplifications from the rigorous

derivation method were applied. [DCA]$^-$ was assigned C_{2v} symmetry (Figure 4), and the G matrix elements for the antisymmetric and symmetric C≡N stretches were obtained and subsequently used in the hyperpolarizability expressions.[44] A brief description of the calculations is available in the Supporting Information.

Simulation curves of peak intensity ratios versus orientational angle θ, as a function of the orientational distribution width, σ, were constructed and plotted simultaneously with the experimental peak ratios obtained from the fits of the spectra. A Gaussian expression was adopted for the distribution.[53,54]

$$f(\theta) = \frac{1}{\sqrt{\pi/2}\,\sigma}\, e^{-(\theta-\theta_m)^2/2\sigma^2} \sin(\theta) \quad (4)$$

From such analysis, a range of possible tilt angles for the symmetry axis of the chemical group under analysis with respect to the surface normal was obtained. The simulation curves are presented in Figures 5a, b, and 6a, b. The ratios of methyl symmetric stretch in ssp polarization with respect to methyl antisymmetric stretch in sps polarization were used for the simulation.

The orientation analysis performed on the [BMIM]$^+$ cation, probed in the C−H stretching region, shows that the C_3 symmetry axis of the methyl group in the butyl chain (Figure 7) has a tilt with respect to the surface normal ranging from 52° to 80° as a function of the distribution width σ ranging from 0° to 30°. This pictures the alkyl chains pointing out to the gas phase. No conclusions can be drawn for the orientation of the imidazolium ring because no ring peaks are observable in the spectra, although this suggests an orientation parallel to the surface of the liquid, a conclusion further supported by the fact that no vibrational peak of the methyl group directly bound to the nitrogen is observed. This is in accordance with previous SFG studies of the ionic liquid/gas interface performed on other compounds based on the imidazolium cation, combined with anions such as halides, tetrafluoroborate, hexafluorophosphate and methyl sulfate,[25,26,42,55,56] and some molecular dynamics simulations that suggest that the ring is oriented parallel to the surface of the liquid.[57,58] The anion (Figure 4), probed in the C≡N stretching region, shows that its C_2 symmetry axis has a tilt ranging from 46° to 90°, for tilt angles ϕ corresponding to the interval of 0° to 30°.

The alkyl chains of the [N6444]$^+$ cation present nearly identical tilt angles: 52° to 80° as a function of σ (from 0° to 30°), for the C_3 axis. Similarly for the anion, the orientation of the C_2 axis ranges from 53° to 90° for tilt angles in the interval of 0−30°, although the signal-to-noise ratio is lower than in the previous case. These results suggest a lesser degree of order regarding the cation alkyl chains of [N6444][DCA] compared
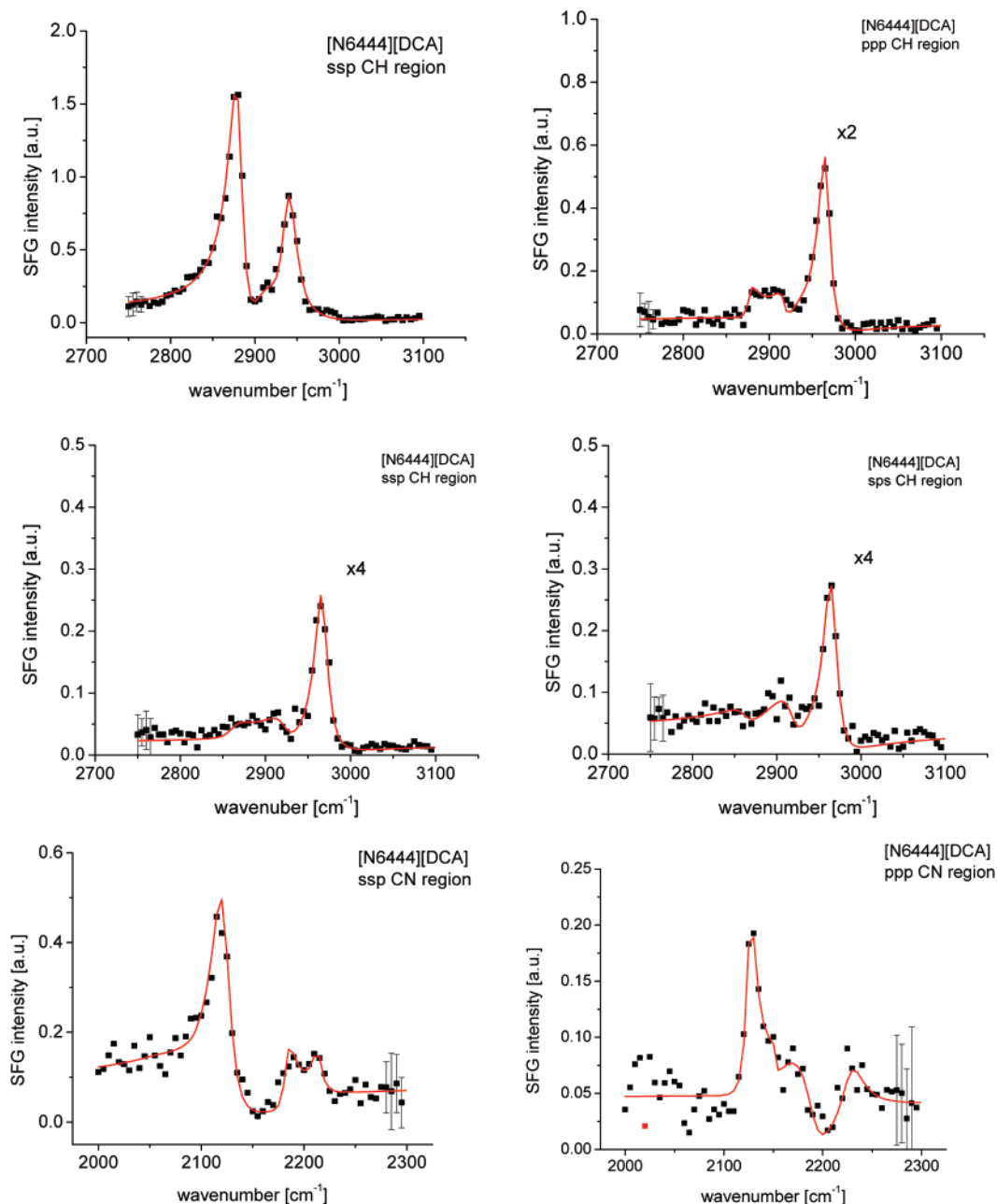
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Figure 3. (a) Sum frequency spectra of [N6444][DCA] at ssp, ppp, sps, and pss polarization combinations for CH stretching region. (b) Sum frequency spectra of [N6444][DCA] at ssp, and ppp polarization combinations for CN stretching region.
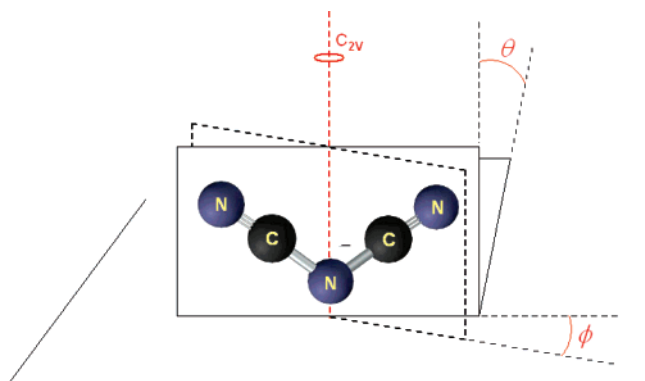

Figure 4. Dicyanamide molecule showing the C_2 axis of symmetry.

to [BMIM][DCA]. In addition, it is not possible to discern, in this case, which alkyl chain is contributing to the signal because of the similarity among the four.

4. Discussion

The interest in the study of the two ionic liquids used in this investigation resides in the fact that [DCA]⁻ is a simple inorganic anion, which can be probed with a vibrational, surface sensitive technique, such as SFG. The advantage of being able to easily probe the [DCA]⁻ anion, allows for comparisons with other systems based on more complex organic/inorganic anions, and may provide insight regarding the surface energy of ionic liquids as a function of the chemical nature of the ions.

4.1. Surface Structure. In a recent study,[56] the structure of the gas/liquid interface of the ionic liquid [BMIM][MS] (where MS stands for methyl sulfate), was studied with SFG. The results indicated that both ionic species occupy the first layer at the gas−liquid interface, and the methyl moieties from both ions were found to be oriented toward the gas phase, which is due to the maximization of the ionic interactions at the interface, thus minimizing the surface energy. That orientation supports
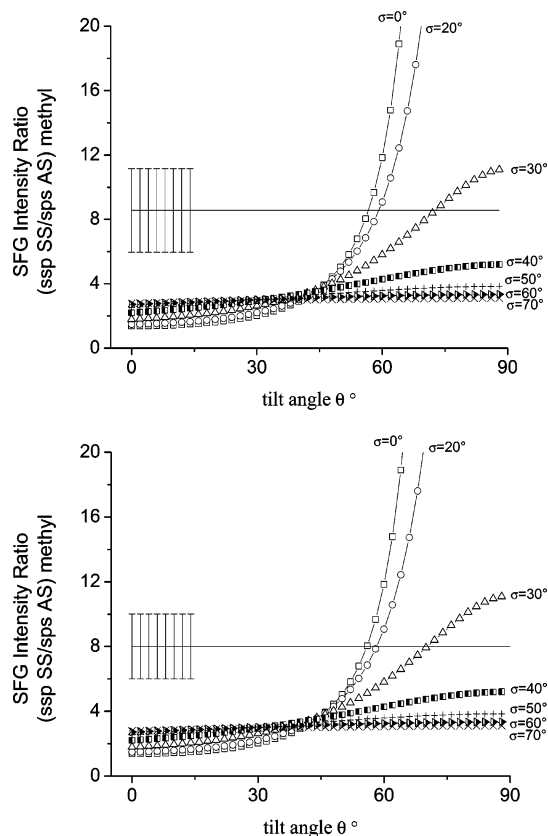
Figure 5. (a) Orientation curve for [BMIM][DCA] in the C−H stretching region as a function of the distribution σ. (b) Orientation curve for [N6444][DCA] in the C−H stretching region as a function of the distribution σ.

Figure 6. (a) Orientation curve for [BMIM][DCA] in the C−N stretching region as a function of the twist angle ϕ. (b) Orientation curve for [N6444][DCA] in the C−N stretching region as a function of the twist angle ϕ.

the concept that in organic liquids, the molecules arrange at the interface in such a way that the more active moieties are directed toward the bulk liquid whereas the least active parts (alkyl groups) are drawn outward to form the surface itself. In that way, the surface energy is taken to a minimum. Since surface tension can be defined as a force per unit length, it is understandable that organic substances show surface tension values on the order of a few tens of mN/m, whereas molten metals or molten inorganic salts possess values approximately an order of magnitude higher.[59,60]

The total surface energy (E^S) and the surface tension are proportional and related by the expression: $\gamma = E^S (1 - T/T_C)$, where γ is the surface tension, T is the temperature, and T_C is the critical point temperature.[60] Furthermore, it is known that the surface tension of a liquid such as water, changes appreciably when organic or inorganic solutes are added. The Gibbs adsorption equation relates the surface tension of a solution with its solute concentration.

$$\Gamma_2^1 = - \frac{c_2}{RT} \frac{d\gamma}{2c_2} = - \frac{1}{RT} \left(\frac{d\gamma}{d\ln c_2} \right) \quad (5)$$

Where Γ_2^1 is the surface excess of the solute, c_2, the molal concentration of the solute in the bulk, and γ is the surface tension. The slope ($d\gamma/d\ln(c_2)$) (negative for organic solutes and positive for inorganic ones) determines if Γ_2^1 will increase or decrease with the concentration of solute in the bulk.[61] This explains the fact that organic compounds tend to reduce the surface tension in aqueous solutions, whereas inorganic compounds increase it.

Since ionic liquids are a solventless medium, the anion must still be present at the interface to prevent the surface from
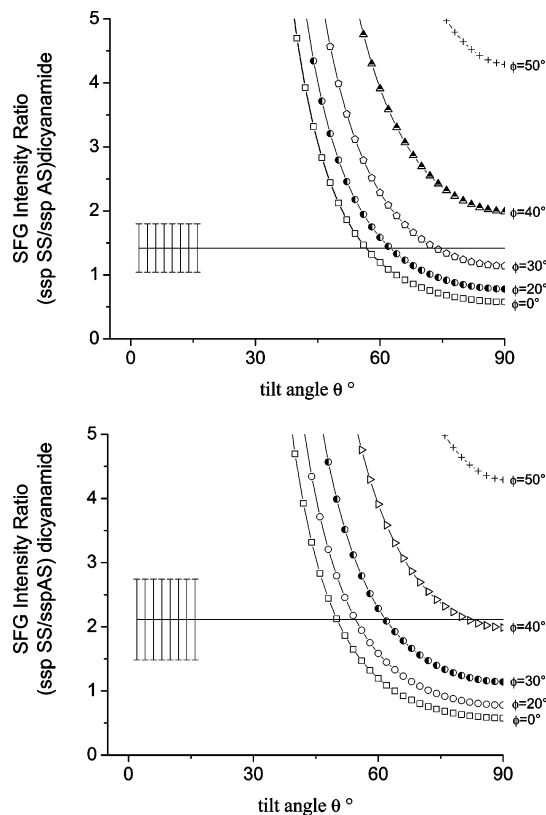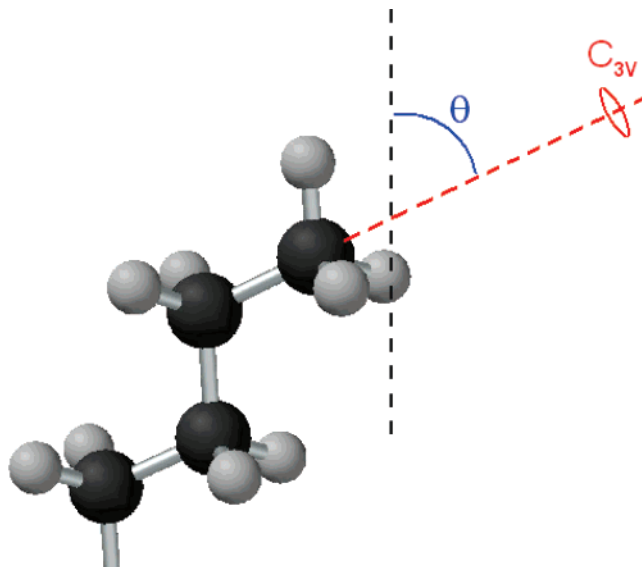

Figure 7. Alkyl chain moiety showing the C_{3v} axis of symmetry and the tilt θ from the surface normal.

developing a large electrical potential. In aqueous systems conversely, this effect is modulated due to hydration.[62] Experimental results on surface tension measurements in aqueous solutions of high surface energy ions, such as simple alkali halides and nitrates, and divalent inorganic anions and/or cations, show a linear increase, and a positive surface excess of anions is found at the surface.[62−64] In contrast, solutions of organic anions such as methanesulfonate, despite showing a similar positive surface excess, show a rapid decay of γ at low bulk concentrations of anion because of the presence of methyl groups which are oriented away from the liquid phase.[65]

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In the work of Sanchez et al.[66] and Rodriguez et al.[67] the surface tension of the ionic liquids [BMIM][DCA] and [BMIM]-[MS] has been measured. The former was studied using the ring method, and the latter was studied using the hanging drop method. The results show greater values for the surface tension of [BMIM][DCA] (48.5 mN/m, versus 44 mN/m for [BMIM]-[MS] at room temperature). This is in accordance with the respective nature of the anion. The inorganic dicyanamide anion causes the liquid to have a higher surface tension compared to methylsulfate.

The simultaneous presence of the cation and the anion as detected in the present investigation is important since the comparison involves interfaces with low surface energy ions versus high surface energy ions. This, added to the surface tension comparison described above, supports the concept that states that inorganic ions increase the surface tension and thus the surface energy of a liquid, whereas organic compounds have the opposite effect. Such a concept, studied in aqueous solutions, is also applicable to solventless liquids such as room-temperature ionic liquids.

Orientation. The SFG orientation analysis suggests that the cation's alkyl chains are oriented at an average angle of 50° from the surface normal. The anion's C_2 axis of symmetry shows slightly higher tilt angles as a function of the twist σ. Despite noticeable differences regarding the signal-to-noise in the SFG spectra of both compounds in the $C\equiv N$ stretch region, there is not a significant difference in the average orientation of the C_2 symmetry axis as calculated with the simulation. A similar conclusion can be drawn concerning the tilt of the C_3 symmetry axis from the alkyl chains in the cation. Concerning the [BMIM]$^+$ ion, the ring seems to lie flat at the surface since no C–H stretch vibrations from the C_4 and C_5 carbon atoms of the imidazolium ring were detected, as well as no peak from the methyl group directly attached to the nitrogen atom. Overall, the vibrational frequencies from the peaks detected in the CN stretch region do not show any clear frequency shift compared to the values measured in the bulk liquid with infrared spectroscopy in the literature.[33,34]

Other surface sensitive techniques were also used to determine the orientation at the surface of ionic liquids based on the 1-butyl-3-methylimidazolium cation. Direct recoil spectrometry at the surface of ionic liquids such as [BMIM][PF$_6$] and [BMIM]-[BF$_4$], as in the work of Watson et al.,[68–70] shows the presence of fluorine, carbon and hydrogen atoms at the interface (the technique being able to probe a depth of 2–4 Å), suggesting that both anion and cation are present at the surface.

Neutron reflectivity was used in the work of Bowers et al.[71] for the compounds [BMIM][BF$_4$] and [OMIM][BF$_4$] (where [OMIM]$^+$ stands for 1-octyl-3-methylimidazolium). A lamellar structure was suggested, formed by segregation between head groups and tail groups, although an unambiguous orientation of the alkyl chains could not be assigned. A similar layered structure was suggested in X-ray reflectivity studies by Deutsch et al.,[72] where two likely molecular arrangements were proposed, one where the alkyl chains are parallel to the surface, and the other with the alkyl chains perpendicular to it. Nevertheless, molecular simulations performed by Lynden-Bell et al.[73] and Balasubramanian et al.[74] for ionic liquids based on [PF$_6$]$^-$, [BF$_4$]$^-$, and [Cl]$^-$ with [BMIM]$^+$ as the cation, suggest that the alkyl chains preferentially orient toward the gas phase and both ions occupy the surface plane.

The results of this study, as well as other SFG spectroscopy experiments,[25,26,56] conducted for imidazolium based ionic liquids, show some differences with the direct recoil spectrom-etry (DRS) results. Experiments with compounds such as [BMIM][BF$_4$], [BMIM][PF$_6$], [BMIM][CH$_3$SO$_4$], [BMIM][CH$_3$-SO$_3$], indicate that the cation ring appears to be lying horizontally at the surface and the alkyl chains pointing toward the gas phase. Nevertheless, there seems to be a good agreement regarding the simultaneous presence of both ions at the surface.[25,42,55,75] Additional studies showed that the anion has little influence on the orientation of the cation for imidazolium-based compounds and that the cation orientation is a function of its symmetry, alkyl chain length, and not a function of the nature of the anion. Moreover, the cation ring was found to lie flat at the liquid surface.[26,56] This agrees with the results of the present investigation as well since similar tilt angles for the alkyl chain were found compared with butylimidazolium ionic liquids based on different types of anions.

Finally, the simultaneous presence of cation and anion at the surface of the dicyanamide-based ionic liquids is also supported by crystallographic data since the features from the bulk structure of the solid-phase resemble those from the surface of an ionic liquid.[76] The crystal structure of ammonium based dicyanamide ionic compounds was determined using neutron powder diffraction and solid-state NMR spectroscopy. Schnick et al.[77,78] reported a structure composed of cations alternating with anions equally spaced and connected by strong and weak hydrogen bonds, forming a zigzag like lattice, where the coordination sphere of an ammonium ion was described as a distorted cube with eight dicyanamide ions at the corners, where six are terminal N and two are bridging amido N.

4.2. Influence of the Cation. The sum frequency spectra in the C–H stretch region do not show any clear differences among the two compounds. However, the same is not true for the anion spectra. The average tilt angle of the anion's C_2 axis is higher for [N6444][DCA]. In addition its overall signal-to-noise ratio seems lower, and the peak ratios show differences with those of [BMIM][DCA]. It is also evident that the intensity of the symmetric stretch is higher for the latter in ssp and ppp polarizations, in accordance with the lower tilt angle. This may be due to difference in size of the cations. [N6444]$^+$ is larger than [BMIM]$^+$, and more spherical in shape as well, which could disrupt the adsorption of the anion at the gas–liquid interface, and therefore, decrease the ordering of the molecules.

5. Conclusion

Sum frequency generation vibrational spectroscopy of the gas–liquid interface was performed for the ionic liquids [BMIM][DCA] and [N6444][DCA]. Both ionic species were detected in each case, and orientational analysis was performed for both compounds. The characteristic vibrational frequencies of the dicyanamide anion make possible the detection of a simple inorganic anion. The tilt angles for the butyl chain in the cation seem in accordance with previous literature values and appear to be pointing toward the gas phase. The tilt angles of the C_2 symmetry axis of the anion were also determined and found to be similar to the angles for the butyl chain. The presence of the anion at the surface supports the higher surface tension values of dicyanamide containing ionic liquids compared to other compounds based on anions that contain lower surface energy, such as alkyl groups.

Supporting Information Available: Normal coordinate analysis, for the derivation of the kinetic energy matrix elements.

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