Raman spectroscopy, ab-initio model calculations, and conformational, equilibria in ionic liquids

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1. Abstract

A review of the recent developments in the study and understanding of room temperature ionic liquids are given. An intimate picture of how and why these liquids are not crystals at ambient conditions is attempted, based on evidence from crystallographical results combined with vibrational spectroscopy and \textit{ab-initio} molecular orbital calculations. A discussion is given, based mainly on some recent FT-Raman spectroscopic results on the model ionic liquid system of 1-butyl-3-methyl-imidazolium ([C\textsubscript{4}C\textsubscript{1}Im]\textsuperscript{+}X\textsuperscript{-}) salts. The rotational isomerism of the [C\textsubscript{4}C\textsubscript{1}Im]\textsuperscript{+} cation is described: the presence of \textit{anti} and \textit{gauche} conformational forms that has been elucidated in remarkable papers by Hamaguchi et al. Such presence of a conformational equilibrium seems to be a general feature of the room temperature liquids. The “localised structure features” that apparently exist in ionic liquids are described. It is
hoped that the structural resolving power of Raman spectroscopy will be appreciated by the reader, when used on crystals of known conformation and on the corresponding liquids, especially in combination with modern quantum mechanics calculations. It is hoped that these interdisciplinatory methods will be applied to many more systems in the future. A few examples will be discussed.

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I. Introduction

Generally room temperature ionic liquids (ILs) consist mostly of ions, e.g. as shown in Fig. 1 {1}. In these liquids the Coulomb interaction plays a major role, in contrast to the situation in ordinary molecular liquids where only dipolar and/or higher order multipolar electrostatic interactions occur. The long-range nature of the Coulomb force tends to make the melting points of ionic crystals much higher than for molecular crystals. The ILs are extraordinary with their low melting points and reasons for this will be considered later.

The intermolecular interactions in ionic liquids are of great importance for their general use, and the basic knowledge in the physical chemistry of these solvent systems is under intensive growth. The number of publications is rising steeply and it is difficult to get an overview. Early studies probed the nature of interactions in so-called first-generation chloroaluminate ionic liquids {2}, and now also information becomes available for second generation, air-stable systems. Many IL studies have covered theoretical aspects {3}, {4}, {5}, {6}, {7} and X-ray crystallography of the frozen melts {8}, {9}, {10}, {11}, {12}, and solubilities of gases in ionic liquids {13}, {14}, {15}.

Hydrogen-bonding is known to occur between the cations and anions in most ionic liquids. As demonstrated by several investigators by e.g. IR and Raman spectroscopy on systems containing 1-alkyl-3-methyl-imidazolium, all three ring protons at C2, C4, and C5, see Fig. 2, form strong hydrogen bonds to halide ions, and the C2 proton is hydrogen bonded to the [BF₄]⁻ anion in neat [C₂C₁Im][BF₄] {16}. The degree of hydrogen bonding between the ring-bound hydrogen atoms and the anion seems to change significantly when going from e.g. a neat chloride to a hexafluorophosphate. IR spectroscopy has provided detailed information on the hydrogen-bonded interaction between water molecules and ionic liquids in e.g. [C₄C₁Im][PF₆] and [C₄C₁Im][BF₄], see {15}, {17}, {18}, {19}.

Raman spectroscopy of [C₄C₁Im]Cl - EtAlCl₂ ionic liquids (Et = ethyl) has shown that the distribution of the ethylchloroaluminate(III) species follows a chlorobasicity pattern similar to that found in alkali chloroaluminate(III) ionic liquids {20}, {21}. Hence, in these ionic liquids Cl⁻ and [EtAlCl₃]⁻ ions are
found when the liquid is chlorobasic. In moderately acidic ionic liquids, EtAlCl$_3$ and [Et$_2$Al$_2$Cl$_5$]$^-$ ions are present, and in highly acidic compositions [Et$_3$Al$_3$Cl$_7$]$^-$ and Et$_2$Al$_2$Cl$_4$ are important components. Similar results are found for [C$_2$C$_1$Im]Cl-Et$_2$AlCl ionic liquid systems {22}. Closer inspection of the Raman spectra of the acidic [C$_2$C$_1$Im]Cl - EtA1C1$_2$ ionic liquids has revealed that the species [AlCl$_4$]$^-$, [EtAl$_2$Cl$_6$]$^-$, Et$_2$AlCl and Et$_3$Al$_2$Cl$_3$ are present {22}. Exchange of ethyl and chloride ligands must be taking place; a quite likely behavior for such complex mixtures.

The ILs interact with surfaces and electrodes {23}, {24}, {25}, and many more studies have been done that what we can cite. As one example, in situ Fourier transform infrared reflection absorption spectroscopy (FT-IRAS) has been utilized to study the molecular structure of the electrified interphase between a 1-ethyl-3-methylimidazolium tetrafluoroborate [C$_2$C$_1$Im][BF$_4$] liquid and gold substrates {26}. Similar results have been obtained by surface enhanced Raman scattering (SERS) for 1-butyl-3-methylimidazolium hexafluorophosphate [C$_4$C$_1$Im][PF$_6$] adsorbed on silver {24}, {27} and quartz {28}. Mixed systems of organic molecules and ionic liquids that form separate phases (by thermomorphic phase separation) have been also studied by Raman spectroscopy {29}.

II. Brief Introduction to Raman Spectroscopy

A. Basics.

The effect of Raman scattering may be defined as instantaneous inelastic scattering of electromagnetic radiation (light) and was discovered in 1928 by Indian physicists Raman and Krishnan {30}, {31}, {32}, {33}. When a photon collides with a sample, it may be elastically scattered (called Rayleigh scattering) or an amount of energy may be exchanged with the sample (Stokes or anti-Stokes Raman processes) as shown schematically in the quantum energy level diagram in Fig. 3. Accordingly, the outgoing photon has less or more energy than the incoming one. A Raman process corresponds to a (fundamental) transition among certain group vibrational states. For the Raman spectral band to occur with a significant intensity, the molecular bond stretching or angle deformation vibration must cause a change in the polarizability of the molecule. The ensemble of light scattering bands constitute the
Raman spectrum. Stokes-shift Raman spectra are most often measured; i.e. the scattered photons have lower frequency than the incident radiation.

Dramatic improvements in instrumentation (lasers, detectors, optics, computers, etc) have during recent years raised the Raman spectroscopy technique to a level where it can be used for "species specific" quantitative chemical analysis. Although not as sensitive as e.g. infrared absorption, the Raman technique has the advantage that it can directly measure samples inside ampoules and other kinds of closed vials because of the transparency of many window materials. Furthermore, with the use of polarization techniques, one can derive molecular information that cannot be obtained from infrared spectra. Good starting references dealing with Raman spectroscopy instruments and lasers are perhaps {34}, {35}, {36}, {37}, {38}.

Raman and Infrared spectroscopies are closely interrelated in that they both depend on characteristic “group” molecular motions in the sample that give rise to the vibrational bands in the spectra. As an example, bands occurring near 2950 cm\(^{-1}\) can often be assigned to aliphatic C-H stretching transitions (although sometimes in “Fermi-resonance” with overtones and other nonfundamental transitions). So-called empirical group frequency charts are available, specifying "fingerprint" bands, that may be used to identify pure materials or the presence of a particular component in a mixture, see e.g. {39}, {40}, {41} and {42}.

During the IR absorption process, a quantum of radiation (a photon) of a particular energy \(E\) and with a frequency \(\nu\) \((E = h\nu)\) is absorbed (\(h\) is Planck’s constant). During the absorption the molecular system undergoes a transition from the ground state (quantum number \(\nu = 0\)) to an excited state \((\nu = 1)\), in the present case e.g. corresponding to a CH\(_3\) group C-H bond stretching with a wavenumber shift of 2900 cm\(^{-1}\). In contrast to this, during Rayleigh and Raman scattering, an exiting photon of much higher energy hits the molecular system and raises it to a virtual state, from where it "immediately" falls back. There are two possibilities, here illustrated with green Ar\(^+\) light of 514.5 nm wavelength corresponding to 19435 cm\(^{-1}\). In so-called Stokes Raman scattering (not so likely), the system falls back to the \(\nu = 1\) state (emitting a 16535 cm\(^{-1}\) photon), or in Rayleigh scattering (more likely) to the \(\nu = 0\) ground state.
(emitting light at \( \sim 19435 \text{ cm}^{-1} \)), producing the so-called Rayleigh wing). If the system is starting from the \( v = 1 \) state (not so likely at room temperature because of the Boltzman distribution), similar transitions can happen. Now also a so-called anti-Stokes Raman process is possible producing photons at \( 22335 \text{ cm}^{-1} \). Most Raman spectroscopy studies report data corresponding to Stokes Raman transitions. Samples (or impurities therein) having energy states near the "virtual" ones (here at e.g. \( \sim 19435 \text{ cm}^{-1} \)) may absorb photons from the incident light and later re-emit the light as a broad intensive background called fluorescence.

Although similar transitional energy ranges occur in IR and Raman spectroscopy, different selection rules govern the intensities in Raman scattering and IR absorption spectra. Hence both types of spectra are often required to fully characterise a substance: A necessary requirement for a molecular motion (such as a vibration, rotation, rotation/vibration, or lattice normal mode) to be measurable in IR spectra it is needed that an oscillating dipole moment is produced during the vibration (in Raman the motion within the molecular system should vary the polarizability). Combinations, differences or overtones of these transitions can occur, but normally only weakly. The selection rules of the transitions are described in quantum mechanics and group theory, see e.g. \{31\}, \{32\}, \{33\}, \{43\} and \{44\}.

**B. Experimental, fluorescence and FT-Raman spectroscopy instrumentation.**

Applications of Raman spectroscopy in analytical chemistry have been limited by the presence of fluorescence from some samples (or from some impurities in the samples). In case of strong fluorescence the use of less-energetic near-IR lasers for the excitation is often a requirement. Fourier-transform Raman instruments have been developed, that successfully apply e.g. \( \sim 1064 \text{ nm} \) laser excitation (from solid state Nd-YAG or Nd-YVO\(_4\) lasers) to avoid the fluorescence \{45\}. The advantage of Raman spectroscopy over IR and other analytical techniques (when the fluorescence problems can be circumvented) stems from the ability of Raman to identify discrete species *in situ*. Raman spectra can be obtained directly from samples of any phase, in e.g. glass cells. With a minimum effort, temperature and pressure limitations can be overcome. The polarization properties of the Raman
scattered light may be employed to select only the isotropic intensity of the symmetric vibrational modes, thereby helping conclusive assignment of the spectra.

The Raman effect is weak, perhaps only $10^{-8}$ of the photons hitting the sample are scattered in Raman. The use of high power lasers (to circumvent the low scattering efficiency) often results in sample decomposition, and fluorescence interference from impurities must be considered a likely problem for visible light. Recent development of charge coupled detectors (CCDs) and notch filters have revolutionized the Raman technique for samples that do not emit much fluorescence. Sampling through a microscope - under high magnification - is an effective way to collect Raman light over a large solid angle, and then only minute sample quantities are necessary.

Room temperature ionic liquids have been the object of several Raman spectroscopy studies but often ILs emit intensive broad fluorescence. In our own experiments, the use of visible laser light (green 514.5 nm or red 784 nm) resulted in strong fluorescence \cite{29}, \cite{46}. Similar observations have been reported for many IL systems. Our experimental spectra needed to be obtained by use of a 1064 nm near-infrared exciting source (Nd-YAG laser at 100 mW of power). The scattered light was filtered and collected in a Bruker IFS66-FRA-106 Raman Fourier-Transform spectrometer equipped with a liquid-N$_2$ cooled Ge-diode detector. Samples were in small glass capillary tubes at $\sim 23^\circ$C. The spectra were calculated by averaging $\sim 200$ scans followed by apodization and fast-Fourier-transformation to obtain a resolution of $\sim 2$ cm$^{-1}$ and a precision better than 1 cm$^{-1}$. The spectra were not corrected for (small) intensity changes in detector response versus wavelength.

### III. Brief Introduction to ab-initio Model Calculations

Ab-initio and semi-empirical Molecular Orbital (MO) model calculations have become an efficient way to predict chemical structures and vibrational (i.e. Raman scattering and IR emission) spectra. We and others have used such approaches to better understand certain features of the spectra, as explained in the following. The basic principles underlying ab-initio model calculations have been described in
many textbooks and papers, see e.g. {44}, {47}, {48}. Applications in relation to ILs and similar systems have also been reported, as discussed later.

The MO calculations may nowadays be performed with e.g. the GAUSSIAN 03W program package {49}. A guessed molecular geometry (conformation) is used as input together with some kind of approximation to the atomic orbitals (so-called basis sets, often sums of Gaussian functions). The total energy is minimized by restricted Hartree-Fock (RHF), Möller Plesset (MP2) or Density Functional Theory (DFT) principles, using e.g. third order Becke-Lee-Yang and Parr (B3LYP) procedures {44}, {48}, {49}. Common basis sets are the split valence 6-31+G(d,p) sets including diffuse orbitals (d) augmented with Pople’s polarization functions (p) {49}. The molecular ions are commonly assumed to be in a hypothetical gaseous free state and without any pre-assumed symmetry, but some calculations also involve better approximations to real systems. After optimization, giving a geometry with a minimum energy – perhaps not a global one - vibrational frequencies and intensities (spectra) and eigenvectors for the normal modes are calculated and displayed on a computer screen, to identify the dominating motions. The frequencies (wavenumbers) are correlated with the Raman and IR bands.

The calculated and experimental vibrational spectra are in more or less good agreement. The wavenumber scale is often calculated as slightly too high, due to the lack of good modelling of the orbitals and interactions with the surroundings. In the gas phase empirical scale factors of ~0.95 are sometimes used to get fairly accurate wavenumber fits. A scaling factor of 1 was used in this work.

IV. Case Study on Raman Spectroscopy and Structure of Imidazolium-based ILs

As mentioned above, vibrational spectroscopy is known to be a very powerful tool in the study of molecular structures and interionic interactions in ILs {18}, {19}, {50}. This is especially so when done in combination with crystal structure studies, as explained in the following.

To illustrate the situation, we start our discussion with the example of the alkyl-methylimidazolium liquids, from $[C_2C_1Im]^+$ to $[C_{18}C_1Im]^+$, and a number of different anions. Although other techniques
such as infrared spectroscopy, X-ray and neutron diffraction studies have been used to study these ions in the liquid or solid state or at surfaces {12}, {51}, {52}, {53}, {54}, {55}, {56}, {57}, {58}, {59}, {60}, {61}, a real gain in our understanding came with the combination of crystal structure solution, Raman spectroscopy and ab-initio DFT calculations {50}, {62}. We concentrate the story on the instructive example of the 1-butyl-3-methylimidazolium cation, $\text{[C}_4\text{C}_1\text{Im]}^+$ (see Fig. 2, without carbon atoms 11 and 12), that makes a number of ILs with varying properties, depending on the different anions. The two prototype ILs $\text{[C}_4\text{C}_1\text{Im]}\text{[BF}_4\text{]}$ and $\text{[C}_4\text{C}_1\text{Im]}\text{[PF}_6\text{]}$ have already been used extensively in fundamental investigations as well as in practical applications. Therefore, the elucidation of their crystal and liquid structures were an important first step for the understanding of ILs in general {50}.

The most fundamental question about ILs to be discussed is: Why are ILs liquids at the ambient temperature, despite the fact that they are composed solely of ions? This question can be answered as described in the following.

$\text{[C}_4\text{C}_1\text{Im]}\text{Cl}$ and $\text{[C}_4\text{C}_1\text{Im]}\text{Br}$ are crystals at room temperature, while $\text{[C}_4\text{C}_1\text{Im]}\text{I}$ is a IL (melting point -72°C {63}). A typical ionic crystal such as NaI only melts at $\sim$660°C. By cooling $\text{[C}_4\text{C}_1\text{Im]}\text{Cl}$ and $\text{[C}_4\text{C}_1\text{Im]}\text{Br}$ liquids below their melting points, supercooled liquids are easily obtained. Crystals could be grown of the $\text{[C}_4\text{C}_1\text{Im]}\text{Cl}$ and $\text{[C}_4\text{C}_1\text{Im]}\text{Br}$ salts and X-ray diffraction used to determine the crystal structures. These systems thus comprised unique systems for studying the structure of the $\text{[C}_4\text{C}_1\text{Im]}^+$ cation in the liquid and crystalline states.

A crystal polymorphism was discovered in the $\text{[C}_4\text{C}_1\text{Im]}\text{Cl}$. It adopts a monoclinic (m.pt. $\sim$41 °C) and an orthorhombic (m.pt. $\sim$66 °C) crystal structure {57}, {58}, {64}, {65}. In the following, we use the Hamaguchi notation "Crystal (1)" and "Crystal (2)". The crystal structures were determined by X-ray diffraction of $\text{[C}_4\text{C}_1\text{Im]}\text{Cl} "\text{Crystal (1)}"$ and $\text{[C}_4\text{ClIm]}\text{Br}$ at room temperature {57} and independently, of $\text{[C}_4\text{C}_1\text{Im]}\text{Cl} "\text{Crystal (1)}"$ and "Crystal (2)", as well as that of $\text{[C}_4\text{C}_1\text{Im]}\text{Br}$ at $\sim$100° C {58}. The structures determined by different authors agreed quite well with each other, taking into account that the lattice constants vary with temperature. The molecular structure of the $\text{[C}_4\text{C}_1\text{Im]}^+$ cation in
[C₄C₁Im]Cl "Crystal (2)" is different from that in (1) but it was the same as that in [C₄C₁Im]Br, as also proved later by the Raman spectra.

The [C₄C₁Im]⁺ cations in the two polymorphs were found predominantly to differ with respect to conformation: The structural results showed that the polymorphism is due to a rotational isomerism of the butyl group of the [C₄C₁Im]⁺ cation around C7-C8, as defined in Fig. 2. In the monoclinic polymorph, the butyl chain is in anti (or trans) conformation around C7-C8, and in the orthorhombic polymorph it is gauche around C7-C8. The conformational difference reveals itself in the rotation of the butyl chain around the C7-C8 bond, that differed by 106.16° between the two conformers {58}. The C8-C9 conformation was found to be anti in both polymorphs. In a convenient and obvious notation, these two conformers of the [C₄C₁Im]⁺ cation are here referred to as the AA and the GA forms (Hamaguchi et al. denote them TT and GT). Also the crystal structure of [C₄C₁Im]Br has been reported {58}.

The crystal structure of the monoclinic [C₄C₁Im]Cl "Crystal (1)" is shown in Fig. 4. Details of structural data are available from the Cambridge Crystallographic Data Centre {66}. The crystal belongs to space group P2₁/n with a = 9.982(10), b = 11.590(12), c = 10.077(11) Å, and β = 121.80(2)°. Both the [C₄C₁Im]⁺ cations and the chloride anions form separate columns extending along the crystal a axis. The imidazolium rings are all planar pentagons. The stretched n-butyl group of the [C₄C₁Im]⁺ cation takes a anti-anti (AA) conformation with respect to the C7-C8 and C8-C9 bonds, as shown in the inset of Fig. 4. The butyl groups stack together (aliphatic interaction) and form columns extending along the a axis, in which all the imidazolium ring planes are parallel with one another. Two types of cation columns with different orientations exist, the planes of the imidazolium rings in the two different columns making an angle of 69.5°. Zig-zag chains of Cl⁻ anions directed in the a direction are accommodated in channels formed by four cation columns, of which two opposite columns have the same orientation. The three shortest distances between Cl⁻ anions in the zig-zag chain were 4.84 Å, 6.06 Å and 6.36 Å and these distances are much larger than the sum of the van der Waals radii of Cl⁻ (3.5 Å). There seems to be no specific interaction among the Cl⁻ anions, and they are likely to be
aligned under the effect of Coulombic forces. The chloride ion is very close to the hydrogen H2 in the
ring (2.55 Å), and to the two methylene protons on C7 (2.72 and 2.73 Å) \{57\}, \{58\}, meeting the
criteria for relatively strong hydrogen bonds \{67\}, \{68\}. Similarly strong hydrogen bonds are observed
in the orthorhombic form \{58\}. Also other crystal structures e.g. of the 1-ethyl-3-methylimidazolium
chloride ([C2C1Im]Cl) \{15\}, the tetrafluoroborate ([C2C1Im][BF4]) and other salts \{69\} have been
reported.

The crystal structure of orthorhombic [C4C1Im]Br (m.pt. 77.6°C \{65\}) is shown in Fig. 5. The detailed
structural data are available from the Cambridge Crystallographic Data Centre \{66\}. The [C4C1Im]Br
crystal belongs to the space group \textbf{Pna2}_1 with $a = 10.0149(14)$, $b = 12.0047(15)$, $c = 8.5319(11)$ Å. As
for the [C4C1Im]Cl "Crystal (1)”, the cations and anions form separate columns extending along the $a$
axis. In [C4C1Im]Br the $n$-butyl group takes a gauche-anti (GA) conformation with respect to the C7-
C8 and C8-C9 bonds (see inset of Fig. 5). Only one kind of cation column is found. The imidazolium
rings are stacked so that the N-C-N moiety of one ring interacts with the C=C portion of the adjacent
ring. The adjacent ring plane can be obtained by rotation of the ring by about 73° around an axis
involving the two N atoms. The zig-zag chain of Br` anions resides in the channel produced by four
cation columns, extending in the $a$ direction. The shortest three Br`-Br` distances (4.77, 6.55, and 8.30
Å) are all longer than the sum of the van der Waals radii (3.7 Å). This indicates that there is no specific
interaction among the Br` anions and that the zig-zag molecular arrangement is a result of Coulombic
interactions.

\section*{V. Raman Spectra and Structure of [C4C1Im]$^+$ Liquids}

The information obtained from the study of the [C4C1Im]$^+$ crystals can be used as a basis to better
understand the liquid structure of the [C4C1Im]X ionic liquids (X is an anion). It is well-known that
Raman spectroscopy facilitates comparative studies of the structures in crystals and liquids. Raman
spectra of [C4C1Im]Cl "Crystals (1) and (2)”, and [C4C1Im]Br by Hamaguchi et al. \{50\}, \{57\}, \{59\},
\{64\}, \{70\} are shown in Fig. 6. As seen, the two polymorphs of [C4C1Im]Cl gave distinct Raman
spectra differing considerably, while those of [C4C1Im]Cl "Crystal (2)” and [C4C1Im]Br were almost
identical. These findings are consistent with the X-ray diffraction experimental results. The halogen anions are inactive in Raman scattering - except for the lattice vibrations, that are observed in the wavenumber region below 200 cm\(^{-1}\) \cite{71}. Therefore, all the Raman bands seen in Fig. 6 can be ascribed to the [C\(_4\)C\(_1\)Im]+ cation. Fig. 6 was accordingly interpreted to indicate that the [C\(_4\)C\(_1\)Im]+ cation takes two different conformations in those salts. To be in accordance with the X-rays results, at least the cation must adopt the same molecular conformation in [C\(_4\)C\(_1\)Im]Cl "Crystal (2)" and [C\(_4\)C\(_1\)Im]Br, and a different one in [C\(_4\)C\(_1\)Im]Cl "Crystal (1)". In this way it emerged that the Raman spectral differences in Fig. 6 most likely originated from the rotational isomerism around the C7-C8 (the AA and GA isomerism) of the butyl chain of the [C\(_4\)C\(_1\)Im]+ cation \cite{64}, \cite{70}.

Raman spectra of liquid [C\(_4\)C\(_1\)Im]X (X = Cl, Br, I, [BF\(_4\)], [PF\(_6\)]) measured at room temperature are shown in Fig. 7. The spectra of [C\(_4\)C\(_1\)Im]Cl "Crystal (1)" and [C\(_4\)C\(_1\)Im]Br are also included for reference purposes. Spectra for fluids [C\(_4\)C\(_1\)Im]Cl and [C\(_4\)C\(_1\)Im]Br were taken from supercooled liquids. The Raman spectra of the [C\(_4\)C\(_1\)Im]X liquids were surprisingly alike. One should note that the Raman spectral bands of the separate [BF\(_4\)]\(^-\) and [PF\(_6\)]\(^-\) anions - that are already well known \cite{41} - have been deleted in Fig. 7. However, from the similarity of the spectra it seems that the structural properties of the [C\(_4\)C\(_1\)Im]+ cation in these liquids are very similar. But what else can be deduced from the spectra?

VI. Normal Mode Analysis and Rotational Isomerism of the [C\(_4\)C\(_1\)Im]+ Cation

To pursue this question further, Ozawa et al. \cite{70} have performed density functional calculations (DFT) with Gaussian98 at the B3LYP/6-31G++ level. In the calculation, the structures of the AA and GA forms of [C\(_4\)C\(_1\)Im]+ were optimized in the vicinity of the determined X-ray crystal structures for [C\(_4\)C\(_1\)Im]Cl "Crystal (1)" and [C\(_4\)C\(_1\)Im]Br, respectively. The structures of the optimized [C\(_4\)C\(_1\)Im]+ cations in the two crystals are depicted in Fig. 8, together with the experimental spectra (in a limited wavenumber region of 1000-400 cm\(^{-1}\)). The calculated fundamental frequencies and intensities were
included in Fig. 8 as thick vertical bars. As seen the calculated “bar”-spectra reproduced the observed spectra quite well.

The normal mode calculation was used to elucidate the rotational isomerization equilibrium of the \([C_4C_1Im]X\) liquids. In the wavenumber region near 800-500 \text{ cm}^{-1}, where ring deformation bands are expected, two Raman bands appeared at \(\sim 730 \text{ cm}^{-1}\) and \(\sim 625 \text{ cm}^{-1}\) in the \([C_4C_1Im]Cl \ "Crystal (1)"\). In the \([C_4C_1Im]Br\) these bands were not found. Here instead, another couple of bands appeared at \(\sim 701 \text{ cm}^{-1}\) and \(\sim 603 \text{ cm}^{-1}\). To assist the interpretation of the spectra, the normal modes of vibrations calculated by Hamaguchi et al. \{50\} are shown in Fig. 9. It shows modes for the \([C_4C_1Im]^+\) ion of the geometry of \([C_4C_1Im]Cl \ "Crystal (1)"\) at 735 \text{ cm}^{-1} and 626 \text{ cm}^{-1}; and similarly the modes for \([C_4C_1Im]Br\) occurring at 696 \text{ cm}^{-1} and 596 \text{ cm}^{-1}. Obviously the 626 \text{ cm}^{-1} band of \([C_4C_1Im]Cl \ "Crystal (1)"\) and the 596 \text{ cm}^{-1} band of \([C_4C_1Im]Br\) originate from similar kind of ring deformation vibrations, but they have different magnitudes of the coupling with the CH2 rocking motion of the C8 carbon (encircled in Fig. 9). It thus seems that more intensive coupling occurs between (i) the CH2 rocking motion and (ii) the ring deformation vibrations in the GA form (596 \text{ cm}^{-1}) than in the AA form (626 \text{ cm}^{-1}), resulting in an overall lower frequency of the mode and therefore a lower wavenumber position of the Raman band \{50\}.

By comparing their normal coordinate analysis results and their liquid experimental Raman spectra in Fig. 7, Hamaguchi et al. \{50\}, \{57\}, \{59\}, \{64\}, \{70\} concluded that the two rotational isomers AA and GA must coexist in the ionic liquid state (AA and GA were called TT and GT by Hamaguchi et al.). According to the Raman spectra of all the liquids in Fig. 7, both of the key bands for the AA conformer (625 \text{ cm}^{-1} and 730 \text{ cm}^{-1} bands), and for the GA conformer (the 603 \text{ cm}^{-1} and 701 \text{ cm}^{-1} bands), respectively, appeared in the spectra. Therefore, the two isomers of rotational freedom around the C7-C8 and C8-C9 bonds - anti-anti and gauche-anti – must coexist in these \([C_4C_1Im]X\) liquids.

Furthermore, the observed relative intensity of the 625 \text{ cm}^{-1} band to that of the 603 \text{ cm}^{-1} band should be correlatable with the AA/GA population ratio of the conformation equilibrium. The observed ratios
depended slightly on the anion: For the halides, it seems to increase in the order \([\text{BF}_4^−] \approx [\text{PF}_6^−] \approx \text{Cl}^- < \text{Br}^- < \text{I}^- \{50\}.

During our work on \([\text{C}_4\text{C}_1\text{Im}]^+\) and \([\text{C}_6\text{C}_1\text{Im}]^+\), we have repeated the experiments and calculations for the \([\text{C}_4\text{C}_1\text{Im}]^+\) cation and found the results of Hamaguchi et al. to be essentially reproducible (details explained in ref. \{46\}). Our calculated Raman spectra in the whole range for the AA (anti-anti) and GA (gauche-anti) conformers of \([\text{C}_4\text{C}_1\text{Im}]^+\) are shown in Fig. 10 and 11. Our assignments (approximate descriptions of the modes giving origin to the Raman bands) are listed in Table 1, based on the calculated vibrational frequencies and we communicate the intensities of the infrared and Raman bands. The movements were depicted on a PC-screen and assignments were derived using the Gaussian03W software.

Our recalculated modes of the \([\text{C}_4\text{C}_1\text{Im}]^+\) cation were obtained with somewhat higher frequencies: the modes at 626, 735, 596 and 696 cm\(^{-1}\) by Hamaguchi et al. in Fig. 9 became 636 and 749 cm\(^{-1}\) for our AA and 622 and 713 cm\(^{-1}\) for our GA modes, see Fig. 12.

According to the calculated minimum energy \(E_e\) of the conformers, the GA was more stable than the AA conformer, but at 298.15 K the Gibbs energy of the AA conformer was 0.168 kJ mol\(^{-1}\) less than that of the GA conformer, indicating 52% of anti-anti versus 48% of gauche-anti or almost equal amounts of the two conformers at equilibrium at room temperature \{46\}. A higher difference between the AA and GA energy was found in other calculations \{73\}. These results are consistent with the observation of both conformers being simultaneously present in the spectra of the \([\text{C}_4\text{C}_1\text{Im}]^+\) liquids as observed by Ozawa et al. \{70\}, see Fig 7.

Our obtained experimental Raman signals for the \([\text{C}_4\text{C}_1\text{Im}]^+\) cation liquids are given in Fig. 13 and the assignments are specified in Table 2, based on the calculations, some of which are summarized in Table 3. Note that bands from the \([\text{PF}_6^-]\) and \([\text{BF}_4^-]\) anions are visible, \(v_1([\text{PF}_6^-])\) symmetric stretching at 741 cm\(^{-1}\), \(v_2([\text{PF}_6^-])\) stretching at 568 cm\(^{-1}\), \(v_3([\text{PF}_6^-])\) symmetric bending at 471 cm\(^{-1}\), \(v_1([\text{BF}_4^-])\)
symmetric stretching at 766 cm$^{-1}$ and $\nu_4([\text{BF}_4])$ bending at 522 cm$^{-1}$ \cite{72}. Similar kind of experimental and calculational results for 

[C$_n$C$_1$Im]X liquids were obtained by Carper and others \cite{74}, \cite{75}, \cite{76}, \cite{77}, \cite{78}.

To conclude the situation for [C$_4$C$_1$Im]$^+$, Ozawa et al. \cite{50}, \cite{70} have discovered - by the combined use of X-ray crystallography, Raman spectroscopy, and DFT calculations - that

- one can use certain Raman bands as key bands to probe the conformation around the C7-C8 bond of the [C$_4$C$_1$Im]$^+$ cation.
- the calculated bands at $\sim$626-636 cm$^{-1}$ and $\sim$735-749 cm$^{-1}$ are characteristic of the AA conformer (anti-anti conformation around the C7-C8 bond), as compared to the experimental values of $\sim$624 and $\sim$730 cm$^{-1}$ (Table 2), whereas the $\sim$596-604 cm$^{-1}$ and $\sim$696-713 cm$^{-1}$ calculated bands are characteristic of the GA conformer (gauche-anti conformation).
- Furthermore a characteristic frequency was calculated as $\sim$504, (Table 1), as compared to the experimental values of $\sim$500, $\sim$602, and $\sim$699 cm$^{-1}$ (Table 2).
- experimentally the Raman spectral bands are occurring at easily recognizable peak positions and with intensities obtainable from ab-initio DFT calculations. Bands measured by Ozawa and Hamaguchi at 701, 625, 603, and 500 cm$^{-1}$ correspond within experimental error to our [C$_4$C$_1$Im][PF$_6$] liquid bands at 698, 624, 601, and 498 cm$^{-1}$ (Table 2).

In a more refined gas phase ion pair model aimed at understanding the interaction in the [C$_4$C$_1$Im][PF$_6$] liquid, Meng et al. \cite{5} in a combined spectroscopic, semi-empirical and ab-initio study, observed hydrogen bonding between the [PF$_6^-$] ion and the hydrogen atom at C2 in the aromatic ring of the [C$_4$C$_1$Im]$^+$ cation. Virtually identical theoretical results were obtained using both Hartree-Fock (HF) and Density Functional Theory (DFT). The DFT minimized structure is shown in Fig. 14. Obviously Meng et al. \cite{5} have reached an anti-gauche (AG) conformation that probably just is local but not a global minimum. The hydrogen bonding has previously been detected by $^{13}$C NMR relaxation studies on [C$_4$C$_1$Im][PF$_6$] and related systems in the liquid state \cite{5}, \cite{6}, \cite{75}, \cite{76}.
It is well known that hydrogen bonding significantly supports the formation of ion pairs (and even higher aggregates) in electrolyte solutions when compared to systems without specific interactions. Hanke et al. \cite{4} in another simulation study found that the largest probability for finding an anion is near C2 below and above the ring. Most likely dimeric and tetrameric ion pairs and higher aggregates are formed with a type of layer structure, in which the anions are located mainly above and below the aromatic ring near C2 \cite{5}, \cite{6}. The occurrence of hydrogen bonding in addition to the Coulombic interactions was put forward to explain the quite high viscosity and other specific macroscopic properties of the \([\text{C}_4\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) ionic liquid.

**VII. Other Studies on \([\text{C}_n\text{C}_1\text{Im}]^+\) Liquids**

Measured IR and Raman spectra of a series of 1-alkyl-3-methyl-imidazolium halides and hexafluorophosphate ionic liquids (\([\text{C}_2\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) to \([\text{C}_4\text{C}_1\text{Im}]\text{[PF}_6\text{]}\)) were correlated with results of \textit{ab-initio} DFT calculations at the 6-31+G* and 6-311+G(2d,p) levels \cite{73}, \cite{74}. It was suggested that common Raman C-H stretching frequencies in these liquids may serve as possible probes in studies of ionic interactions. Hydrogen bonding interactions were observed between the fluorine atoms of the \([\text{PF}_6\text{]}^-)\) anion and the C2 hydrogen on the imidazolium ring, and between \([\text{PF}_6\text{]}^{-}\) anion and the H atoms on the adjacent alkyl side chains. There are at least four discernible strong vibrations in the 2878 to 2970 cm\(^{-1}\) region of the \([\text{C}_2\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) Raman spectrum \cite{74}. These Raman vibrations are represented by the calculated vibrations in the 3153 to 3220 cm\(^{-1}\) region and represent a complex combination of multiple stretching and bending vibrations. The weak Raman bands observed at 3116 and 3179 cm\(^{-1}\) were assigned to vibrations associated with the imidazolium ring (H-C-C-H and N-(C-H)-N) C-H stretches.

Similar studies were done on \([\text{C}_2\text{C}_1\text{Im}]\text{[BF}_4\text{]}\) and other 1-ethyl-3-methylimidazolium liquid salts \cite{16}, \cite{69}, \cite{79}, \cite{80}. In the Raman spectral range 200-500 cm\(^{-1}\), Umebayashi et al. \cite{80} for liquids
containing \([\text{BF}_4]^-\), \([\text{PF}_6]^-\), \([\text{CF}_3\text{SO}_3]^-\), and \([(\text{CF}_3\text{SO}_2)\text{N}]^-\) found bands at 241, 297, 387, 430, and 448 cm\(^{-1}\) that must originate from the \([\text{C}_2\text{C}_1\text{Im}]^+\) ion. However, the 448 cm\(^{-1}\) band could not be reproduced by theoretical calculations in terms of a single given \([\text{C}_2\text{C}_1\text{Im}]^+\) conformer. The ethyl group bound to one N atom of the imidazolium ring is able to rotate around the C-N bond to yield two different torsion conformers, see Fig. 15. The energy barrier of this rotation was calculated with an energy amplitude of \(\sim 2\) KJ mol\(^{-1}\) \(^{(80)}\). Two local minima were found, suggesting that the two conformers can be present in equilibrium. Full geometry optimizations followed by normal frequency analyses indicated that the two conformers of minimum energy were those with planar and nonplanar ethyl groups against the imidazolium ring plane, and that the nonplanar conformer was the most favorable. The Raman bands at 241, 297, 387, and 430 cm\(^{-1}\) were found to mainly originate from the nonplanar conformer, whereas the 448 cm\(^{-1}\) band originated from the planar conformer. Indeed, the enthalpy for conformational change from nonplanar to planar \([\text{C}_2\text{C}_1\text{Im}]^+\), obtained experimentally by analyzing band intensities of the conformers at various temperatures, was practically the same as the enthalpy evaluated by the theoretical calculations. We thus conclude that the \([\text{C}_2\text{C}_1\text{Im}]^+\) ion exists as planar or nonplanar conformers in equilibrium in its liquid salts \(^{(80)}\), and this was confirmed by X-ray diffraction \(^{(69)}\). For the longer chain \([\text{C}_n\text{C}_1\text{Im}]^+\) systems also non-planar forms are most stable, e.g. compare with the AA and GA conformers of \([\text{C}_4\text{C}_1\text{Im}]^+\) in Fig. 9.

We have shown \(^{(46)}\) that the same situation as for \([\text{C}_4\text{C}_1\text{Im}]^+\) exists for longer alkyl chain systems, at least for the 1-hexyl-3-methylimidazolium cation. Raman spectra for \([\text{C}_6\text{C}_1\text{Im}]^+\) cation systems have bands at 698, 623, and 601 cm\(^{-1}\)(but no distinct band at \(\sim 498\) cm\(^{-1}\)). A comparison between typical experimental spectra is shown in Fig. 16. Also the calculations came out in much the same way, as can be seen by comparing the results in Fig. 17 with those from Fig. 11 (insets).

All in all, it was recognised, both from spectra and calculations that the characteristic frequencies do not change significantly when the butyl group was exchanged for a hexyl group, and we conclude that the AA - GA isomerism phenomenon probably is general, and not specific to the \([\text{C}_4\text{C}_1\text{Im}]^+\)X ionic liquids. For a discussion of the hexyl systems we refer to our comprehensive report \(^{(46)}\).
VIII. Conformations Equilibria in Liquids versus Temperature

The Raman spectra of \([C_nC_1Im][BF_4]\) from \(n = 10\) to \(n = 2\) in the liquid state at room temperature are shown in Fig. 18. Clearly the rotational isomerism around C7-C8 interconvert the AA and GA conformers so as to change the AA/GA ratio with the cation. For \([C_2C_1Im][BF_4]\) there can be no rotational isomerism around C7-C8 because C8 is the end methyl group \(\{16\}\) and only one Raman band is observed at 596 cm\(^{-1}\), corresponding to the band from the GA conformation of \([C_4C_1Im][BF_4]\). This observation was rationalized by Hamaguchi et al. \(\{50\}\) who noted that the methyl rocking motion of the C8 carbon is strongly coupled to the ring deformation vibration and pushes down the frequency in \([C_2C_1Im]^+\) exactly as in the case of the GA conformation of the \([C_4C_1Im]^+\) cation.

For longer side-chains, the 625/603 cm\(^{-1}\) Raman intensity ratio increases with increasing \(n\) because the all-anti AA..... kind of band at 625 cm\(^{-1}\) grows in intensity. Since the vibrational modes are very similar - being localized within the imidazolium ring and around the C7 and C8 carbons (see Fig. 12) - their Raman cross sections are thought to be quite independent of the chain length \(\{46\}\). Therefore, the 625/603 cm\(^{-1}\) Raman intensity ratio can be regarded as a direct measure of the AA.../GA... isomer ratio. The observed increase of the 625/603 cm\(^{-1}\) intensity ratio with \(n\) means that the AAA.../GAA... isomer ratio increases as the chain becomes longer. The AAA... structure stabilization relatively to the GAA... one for longer alkyl chains is understandable only if we assume interactions among the cations. Otherwise, the relative stability would be determined alone by the energy difference between the anti and gauche conformations around the C7-C8 bond and would be likely to be independent of the chain length. Instead, the AA.../GA... ratio dependence of the chain-length therefore must depend on aliphatic interactions between the alkyl chains. In Fig. 18, the broad CH\(_2\) rocking and bending features observed for longer-chain \([C_nC_1Im][BF_4]\) liquids (\(n = 7\)-10) in the region near 800-950 cm\(^{-1}\), are indicative of such interactions between the alkyl chains \(\{50\}\), similar to the interactions found for certain meso-phase liquid crystals when \(n > 12\), see \(\{12\}, \{55\}, \{81\}\).
An unusually long equilibration time has been observed upon melting of a single crystal of the AA polymorph of [C₄C₁Im]Cl "Crystal (1)" heated rapidly from room temperature to 72°C to form a droplet of liquid in a non-equilibrium state {50}. Raman versus time spectra are reproduced in Fig. 19. Before melting and for some time after only the band at 625 cm⁻¹ of the AA [C₄C₁Im]^+ cation was observed in the 600 to 630 cm⁻¹ region. Gradually 603 cm⁻¹ band due to the GA conformer became stronger. After about 10 min. the AA/GA intensity ratio became constant. The interpretation {50} is that the rotational isomers do not interconvert momentarily at the molecular level. Most probably it involves a conversion of a larger local structure as a whole. The existence of such local structures of different rotamers has been found by optical heterodyne-detected Raman-induced Kerr-effect spectroscopy (OHD-RIKES) {82}, Coherent anti-Stokes Raman scattering (CARS) {83}, neutron scattering and diffraction experiments {54}, {53}, and by theoretical molecular dynamics calculations {4}, {7}, {84}, {85}.

The enthalpy difference between the AA and GA conformers in the 1-butyl-3-methylimidazolium tetrafluoroborate ILs is much smaller than the corresponding enthalpy difference between the conformers of a free butane chain. This indicates that the 1-butyl-3-methylimidazolium cations most likely form local liquid structures specific to each rotational isomers {50}. Coexistence of these local structures - incorporating different rotational isomers - seems to hinder the crystallization. This is probably the reason for the low melting points of such ILs.

These local structures most probably distinguish ILs from conventional molecular liquids and may explain why ILs phases are between a liquid and a crystal.

**IX. Local Structures in Ionic Liquids**

From NMR spectroscopy it is known that conformational isomers of alkane chains give coalesced peaks indicating transformation between the conformers taking place much faster than a second. Accordingly, one should expect single [C₄C₁Im]^+ cations undergoing AA to GA transformation almost
instantaneously \{86\}. The observed ~10 min. long equilibration time in liquid [C₄C₃Im]Cl (Fig. 19) therefore has been taken to indicate that the conformers do not transform at the single molecular level but only interconvert through slow collective transformations of ensembles of [C₄C₃Im]+ cations (analogous to a phase transition) \{50\}, \{86\}. Most probably the two rotational isomers are incorporated in specific local structures tending to interconvert only through conversion of the local structures as a whole and giving rise to wide pre-melting ranges and other features \{65\}.

The ordering of the anions in ionic liquids has - for the case of [C₄C₃Im]I - been confirmed by large-angle x-ray scattering experiments \{59\}. In this way it seems that the zig-zag chains found in the [C₄C₃Im]X crystals do exist in the ionic liquid state as well, at least partially. Thus, by combining Raman spectroscopy with several other experimental and theoretical techniques, Hamaguchi and coworkers have come to mean that both the cations and anions in [C₄C₃Im]X ILs might have local ordering of their structures. Their conceptual structure of ionic liquids is reproduced in Fig. 20.

According to the model, the supposed local structures are positioned and oriented randomly, and there seems to be no translational and orientational order at the macroscopic level. The local structure modelling of Ozawa and Hamaguchi for the [C₄C₃Im]X ILs is shown in Fig. 20 (e) in comparison with the structures of a crystal (a), liquid crystals (b and c), and a conventional liquid (d). In the crystal (a), component molecules or ions are arranged to form a periodic lattice with long-range order. In a standard liquid state (d), the molecules or ions take random positions and random orientations and there is no order. In liquid crystals (b and c), different kinds of long-range order exist, with e.g. only partial orientational order (b) or random position (c).

In [C₄C₃Im]X ILs, the supposed "local structures" are positioned and oriented randomly, and there seems to be no translational and orientational order at the macroscopic level. Taking into account that the [C₄C₃Im]X ILs are all transparent (not opaque), the dimension of those “local structures” must be much smaller than the wavelength of visible light (<100 Å) \{50\} \{86\}. 20
Microphase segregation in imidazolium-based ionic liquids has also been discussed, and the existence of polar and nonpolar microsegregated domains in ionic liquids has been predicted in molecular simulation dynamics \cite{87}. The structural analysis helps the understanding of solvation of nonpolar, polar, and associating solutes in these media \cite{53}, \cite{87}. The existence of an extended hydrogen-bonded network structure was suggested by Abdul-Sada et al. \cite{88} for 1-alkyl-3-methylimidazolium halides based on results from fast-atom bombardment mass spectroscopy. Charge ordering in ILs was discussed by Hardacre et al. \cite{53}. They obtained the radial distribution curves of dimethylimidazolium chloride and hexafluorophosphate liquids using neutron diffraction and argued for charge ordering of ions in ILs resembling what is found in the solid state. Charge ordering has also been discussed in a number of molecular dynamics computer simulation studies on 1-alkyl-3-methylimidazolium-based ILs in recent few years \cite{7}, \cite{84}, \cite{85}, \cite{89}, \cite{90}, \cite{91}, \cite{92}, \cite{93}, \cite{94}, \cite{95}, \cite{96}, \cite{97}, \cite{98}, \cite{99}. The radial distribution functions calculated in these papers all have suggested long-range charge ordering, giving support to the idea that ILs are unique in having more structure ordering than do conventional molecular liquids.

Many unique properties may be expected to arise from these local structures in ILs. One example is the\textit{ unusually high viscosity} of certain ILs arising from the hindering of the translational motion of the ions. Magnetic behavior is another most unusual and interesting property that arise when magnetic ions (strongly interacting with one another) are locally aligned in a liquid. Recently it was demonstrated \cite{100}, \cite{101} that \textit{magnetic} ILs can be made by mixing imidazolium chlorides ([C\textsubscript{4}C\textsubscript{1}Im]Cl or [nC\textsubscript{4}C\textsubscript{1}Im]Cl) and FeCl\textsubscript{3}, forming 1-butyl-3-methylimidazolium tetrachloroferrate [C\textsubscript{4}C\textsubscript{1}Im][FeCl\textsubscript{4}] and 1-butyronitrile-3-methylimidazolium tetrachloroferrate [nC\textsubscript{4}C\textsubscript{1}Im][FeCl\textsubscript{4}] (IUPAC name of [nC\textsubscript{4}C\textsubscript{1}Im]\textsuperscript{+} cation: 1-(3-cyanopropyl)-3-methyl-1\textsubscript{H}-imidazol-3-ium). These nearly paramagnetic liquids show strong responses to magnetic fields, probably because of local ordering of the magnetic high-spin [FeCl\textsubscript{4}]\textsuperscript{-} anions. The surfaces of the liquids bend (deviate from being horizontal) when they are approached by a magnet, an interesting property that might find applications. FT-Raman spectroscopy indicated that the magnetic liquids contained [C\textsubscript{4}C\textsubscript{1}Im]\textsuperscript{+} and [nC\textsubscript{4}C\textsubscript{1}Im]\textsuperscript{-} cations. The constitution of the liquids thus were confirmed by their Raman spectra. By combining many different cations and
magnetic anions it might be possible to prepare superparamagnetic or even ferromagnetic ionic liquids \cite{100}, \cite{101}.

Another interesting behavior of an ionic liquid has been observed: The molecular arrangements of 1-butyronitrile-3-methylimidazolium halides, in the presence and absence of intruded water molecules, form a new kind of ice that has been studied by Raman spectroscopy \cite{102}, \cite{103}. Single crystals of the ice were isolated and the structure elucidated by single-crystal X-ray crystallography. Apparently the water changes the physical properties of the ionic liquid at the molecular level and this was found to change the conformation of the \textit{n}-butyronitrile chain of the cation. The hydrogen bonding interaction between the anion and the water molecule seems to lead to loose molecular packing arrangements of the IL. As the unique properties are related to the structures and molecular arrangements of the ILs, the presence of water, wanted or unwanted, must be carefully examined in any kind of IL research and applications \cite{103}.

X. Other systems
Raman spectra of N-butylpyridinium chloride - aluminum trichloride liquid systems (e.g. \textcolor{red}{[C\textsubscript{4}py][AlCl\textsubscript{4}]}, Fig. 1) were obtained at ambient temperatures already in 1978 \cite{104}. The \textcolor{red}{[C\textsubscript{4}py][FeCl\textsubscript{4}]} also is a IL, and in the phase diagram of the binary system \textcolor{red}{[C\textsubscript{4}py]Cl - FeCl\textsubscript{3}} liquids are formed in a wide mol fraction composition range from 0.26 to 0.58 \cite{105}. Unrestricted HF calculations were performed with 6-31G* basis sets in order to predict the structures, energies, bond lengths, and vibrational (Raman) frequencies. Both the Raman scattering experiments and the \textit{ab-initio} calculations indicate that \textcolor{red}{[FeCl\textsubscript{4}]^-} is the predominant anion in the ionic liquid at a mole fraction of 0.50 \cite{105}.

The structure of the bis(trifluoromethylsulfonyl)imide ([Tf\textsubscript{2}N]^-) anion in the liquid state has been investigated by means of IR and Raman spectroscopy and \textit{ab-initio} self-consistent Hartree-Fock and DFT calculations on the free ion, aiming at a determination of the equilibrium geometry and understanding of the vibrational spectrum \cite{80}, \cite{89}, \cite{90}, \cite{106}, \cite{107}, \cite{108}. A pronounced
delocalization of the negative charge on the nitrogen and oxygen atoms was found, and a marked double-bond character of the S-N-S moiety for the anion \{106\}, \{107\}. A tentative assignment of some characteristic vibrations of the [Tf$_2$N] anion was performed using the spectra of aqueous solutions for comparison in order to analyze the conformational isomerism and ion-pairing effects \{106\} \{107\}. Also it was found that dihedral S-N-S-C torsion angle in the bistriflylimide anion, has a complex energy profile which was precisely reproduced when tested by confrontation against liquid-phase Raman spectroscopic data \{89\}, \{90\}, \{91\}.

The Raman spectra of the [C$_2$C$_1$Im][Tf$_2$N] show relatively strong bands arising from the [Tf$_2$N]$^-$ ion at $\sim$398 and $\sim$407 cm$^{-1}$, see Fig. 21 \{108\}. Interestingly, the $\sim$407 cm$^{-1}$ band, relative to the $\sim$398 cm$^{-1}$ one, grows appreciably in intensity with raising temperature. This feature is suggesting that an equilibrium is established between [Tf$_2$N]$^-$ conformers in the liquid state, see Fig. 22. According to the DFT calculations (followed by normal frequency analyses), two conformers (of C$_2$ or C$_1$ point group symmetry; two-fold rotational axis or no symmetry, respectively) constitute global and local minima, and have an energy difference of 2.2-3.3 kJ mol$^{-1}$ \{108\}. The observed spectra over the range 380-440 cm$^{-1}$ could be understood from the calculation of [Tf$_2$N]$^-\text{ conformers: The omega-SO}_2$ wagging vibration appeared at 396 and 430 cm$^{-1}$ for the C$_1$ conformer and at 387 and 402 cm$^{-1}$ for the C$_2$ one. The enthalpy of the conformational change from the most stable C$_2$ to C$_1$ came out in good agreement with the theoretical calculation. It was concluded that a conformational equilibrium indeed must exist between the C$_1$ and C$_2$ conformers of [Tf$_2$N]$^-$ in liquid [C$_2$C$_1$Im][Tf$_2$N] \{108\}. Three different conformers (named cis and trans by the authors) have recently been found in the X-ray crystal structure of the salt Li$_2$[C$_2$C$_1$Im][Tf$_2$N]$_3$ \{109\}.

We were able to obtain the same wagging omega-SO$_2$ vibrational bands in our Raman spectrum of liquid [C$_4$C$_1$Im][Tf$_2$N], see Fig. 23. Apparently the splitting between the two bands (at 411 and 403 cm$^{-1}$) is not so large for the case of the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide liquid. The symmetric CF$_3$ stretching and deformation bands are seen very strongly at $\sim$1242 and $\sim$742 cm$^{-1}$ in our spectra, as found also by Rey et al. \{106\}, \{107\}. The bands at 500-750 cm$^{-1}$ discussed in
relation with Fig. 7 can be faintly seen, showing that the AA/GA conformational equilibrium of the butyl group in [C4C1Im]+ is established, as discovered by Hamaguchi et al. {50}.

The [Tf2N]- anion was further studied and discussed in Raman investigations on the ionic liquid N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([P13][Tf2N]) and its 2/1 mixture with Li[Tf2N] {110}, as well as on the N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([P14][Tf2N] or [4-C1C4py][Tf2N]) and other useful reaction media such as [4-C1C4py][TfO] {111}, {112}. Raman results have also shown that [Tf2N]- anions only interact weakly with [P13]+ cations, but coordinated strongly to Li+ cations over a temperature range extending from -100 to +60 °C, i.e. in the crystalline and melt states {113}.

By means of Raman spectroscopy and DFT calculations on the [4-C1C4py][Tf2N] and [4-C1C4py]Br systems, various types of conformations with respect to the pyrrolidinium ring and N-butyl group were found {113}. The calculations indicated that, among others, the so-called eq- and ax-envelope conformers with the butyl group at equatorial and axial positions, respectively, against the plane of four atoms of the envelope pyrrolidinium ring (see Fig. 24) were relatively stable, and the former gave the global minimum {113}.

By comparing observed and calculated Raman spectra it was found that the [4-C1C4py]+ ion was present mainly as the ax-envelope conformer in the [4-C1C4py]Br crystal, while the eq- and ax-envelope conformers were present in equilibrium in the [4-C1C4py][Tf2N] ionic liquid (called [P14][TFSI] {113}). The presence of conformational equilibria was further experimentally supported by Raman spectra measured at different temperatures. It was established that the conformation of the butyl group was restricted to a so-called trans-TT conformation, in which the butyl group is located trans against a ring carbon atom (C2 or C5), and all carbon atoms in the butyl chain are located trans to each other {113}.
We have briefly investigated some [4-C$_1$C$_4$py]$^+$ room temperature liquids, namely [4-C$_1$C$_4$py] Tf$_2$N\) and \([4-C_1C_4py][\text{TfO}]\) \cite{72}. The experimental Raman spectra of our liquids looked much like \textit{sums} of the spectrum of the \([\text{bmpy}]^+\) ion (as measured from the chloride salt) and the spectra of the \([\text{Tf}_2\text{N}]^-\) or \([\text{TfO}]^-\) ions (as measured from the lithium salts). An example of our results on \([4-C_1C_4py][\text{Tf}_2\text{N}]\) is shown in Fig. 25. The spectra in Fig. 25 clearly show that the constituent ions in the liquid and in the respective solid salts vibrate \textit{rather} independent of the surroundings. Therefore the liquid spectrum looks much like the sum of the solid salts. This conclusion is of course not new, but never the less it is still \textit{quite} applicable in the evaluation of many IL Raman (and IR) spectra. However, the presence of conformational equilibria for both of the IL ions makes a closer study worth while. We therefore recommend the interested reader to study the work by Umebayashi et al. \cite{113}, in which subtle spectral band shape details e.g. around 930-880 cm$^{-1}$ are evaluated to show information on the \textit{eq-envelope:trans-TT} and \textit{ax-envelope:trans-TT} interconversion of the \([\text{bC1Im}]^+\) ion in the liquid. Also note that the crystal structure of the \([4-C_1C_4py][\text{Tf}_2\text{N}]\) salt was recently solved; it contained the \textit{eq-envelope:trans-TT} conformer of the cation \cite{114}. Also conformers of symmetry C$_1$ and C$_2$ of the \([\text{Tf}_2\text{N}]^-\) ion show their presence buried in the band at 400-440 cm$^{-1}$ \cite{108}.

Prior to the publication of the work by Umebayashi et al. \cite{113} on the 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide, some preliminary calculations were done aiming at a better understanding of the spectra on that system (shown in Fig. 25). To illustrate how useful such procedures are, we depict two examples of our own results in Fig. 26. The shown \textit{ax-envelope:trans-TG} and \textit{-TT} conformations are just some of the many possible conformations. The more likely ones, such as the \textit{ax-envelope:trans-TT} and \textit{eq-envelope:trans-TT} were included in the study by Umebayashi et al. \cite{113}. The calculated spectra of the different conformers looked rather much like each other. As seen in Fig. 26 the \textit{gauche} form of the C8-C9 bond did not change much relative to the \textit{ax-envelope:trans-TT} form. Quite satisfactory one-to-one correspondences between calculated and observed bands are found in Fig. 26 and also in the work of Umebayashi et al. \cite{113}. One should not expect perfect fits (frequencies are calculated too high and intensities are perturbed, because of the simplicity of the modelling).
When the theoretical spectra of the [4-C₄py][Tf₂N]⁺ ion (e.g. those in Fig. 26) and similarly calculated spectra of conformations of the [Tf₂N]⁻ ion (in Fig. 27, see later) were added, we obtained sums (not shown) that essentially corresponded to the spectrum of the [4-C₄py][Tf₂N] liquid (in Fig. 25, top) {72}.

New 2-hydroxypropyl-functionalized imidazolium cation ionic liquids (containing an appended hydroxyl functionality) have been made {115} by use of an “atom efficient one-pot reaction” between 1-methylimidazole and acid with propylene oxide. Unfortunately the systems were not studied by FT-Raman spectroscopy so far. We have shown in a study on 1-hexanol in [1,3-bis-[2-(methoxyethoxy)ethyl]imidazolium] bis-trifluoromethylsulfonyl-imide {29} that Raman spectroscopy has a potential for finding clues to what goes on in ionic liquids that contain hydroxyl groups (alkohols) and where hydrogen bonding between the ionic liquid and the hydroxyl group is of importance.

A rather new class of room temperature ionic liquids is based on the N,N,N',N'-tetramethylguanidinium [((CH₃)₂N)₂CNH₂]⁺ or [TMGH]⁺ cation, see Fig. 1. A dedicated force field was developed {116} to fit the experimental bonds and angles and the vibration frequencies, for five kinds of [TMGH]⁺ ILs, where the anion was formate, lactate, perchlorate, trifluoroacetate, and trifluoromethylsulfonate, respectively. Ab-initio calculations were performed and predictions in good agreement with the experimental data obtained. Radial and spatial distribution functions (RDFs and SDFs) were investigated to depict the microscopic structures of the ILs {13}.

An illustrative FT-Raman spectrum was recorded on the [TMGH][Tf₂N] liquid to be compared with calculated spectra of the constituent isolated ions in their equilibrium geometries obtained at the RHF/6-31G(d) level using DFT/B3LYP methods {49}. Some data obtained {72} are shown in Fig. 27. Unfortunately the highest-frequent N-H stretchings were out of our instrumental range (limited to 3500
– 100 cm$^{-1}$). However, many experimental details are being convincingly accounted for by the modelling, just by summation of the calculated spectra, even when other conformers are left out.

**XI. Other Applications of Raman Spectroscopy**

Raman spectroscopy has up to now mainly been applied to elucidate conformational forms and associated conformational equilibria of the ionic liquid components. Yet other applications are appearing in these years. One example is the characterization of metal ions like Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ in coordinating solvent mixtures by means of titration Raman Spectroscopy {117}. Another issue is the study of solvation of probe molecules in ionic liquids. In such a study {117}, e.g. acceptor numbers (AN) of ionic liquids in diphenylcyclopropenone (DPCP) were estimated by an empirical equation associated with a C=C / C=O stretching mode Raman band of DPCP. According to the dependence of AN on cation and anion species, the Lewis acidity of ionic liquids was considered to come mainly from the cation charge {118}.

Finally Raman spectroscopy has a potential of being used for qualitative and quantitative analysis. We have used Raman spectroscopy to verify the presence of components in a two-phase system {29}.

**XII. Conclusions**

Recently Raman spectroscopy has been applied - in combination with other methods - to show that certain characteristic spectral bands can be identified that are characteristic for conformational forms (conformers) of the ionic liquid components, and that the associated conformational equilibria might be partly responsible for the salts to have such low melting points.

In this review we have discussed in detail some examples of the conformational equilibria, e.g. those discovered by Hamaguchi, *et al.* {70} in liquids containing the 1-butyl-3-methylimidazolium cation. Also, we have examined in some detail liquids containing the bis(trifluoromethanesulfonyl)imide anion, as described above. We have extended the knowledge on the characteristic Raman bands to include conformers of the 1-hexyl-3-methylimidazolium cation {46}. Vibrational analysis has been
made of the components of the systems to improve our understanding of what goes on in the liquids. These results, although not surprising, add weight to our understanding of the existence of mixtures of low symmetry conformers that disturb the crystallisation process. Arguments have been presented for the belief that this is the reason for the low melting points of the ILs relative to “normal molecular salts” with much higher melting points.

We have seen that the ab-initio self-consistent quantum mechanical functional methods such as e.g. DFT/B3LYP with the chosen 6-31+G(d,p) basis sets are well suited to calculate reasonable molecular ion structures and vibrational spectra of these ions. The results obtained by us or others have indicated that the neglect of the presence of cation-anion interactions is a reasonable approximation for a rather successful prediction of the Raman spectra. Based on such calculations detailed and reliable assignments of the spectra can be given and information on conformational equilibria obtained.

XIII. Acknowledgements

I would like to thank Niels J. Bjerrum, Anders Riisager, Rasmus Fehrmann and Irene Shim from Department of Chemistry, DTU, Denmark, Cory C. Pye from Department of Chemistry, Saint Mary’s University, Halifax, Nova Scotia, Canada, N. Llewellyn Lancaster from Department of Chemistry, King’s College, London University, UK, Ken Seddon, QUILL Research Centre, Queen’s University Belfast, Northern Ireland, Mihkel Koel from Department of Chemistry, Tallin University of Technology, Estonia, and Susanne Brunsgaard Hansen (formerly from Department of Chemistry, DTU) for help with finishing the manuscript. Lykke Ryelund and Ole Faurskov Nielsen of the Department of Chemistry, H.C. Ørsted Institute, University of Copenhagen are thanked for much measurement assistance. The work was supported by the Technical University of Denmark.
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{66} Cambridge Crystallographic Data Centre, [C4mim]Cl ”Crystal (1)” and [C4mim]Br data are registered as CCDC deposition number 213959 and 213960, respectively, see http://www.ccdc.cam.ac.uk.


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**Table 1.** Approximate descriptions* of vibrational frequencies (IR and Raman bands) as determined in MP2 calculations for the [C₄C₁Im]⁺ cation with the butyl group either in the AA (anti-anti) conformation or in the GA (gauche-anti) conformation, derived from movements as depicted on a PC-screen.

<table>
<thead>
<tr>
<th>Mod e</th>
<th>butyl group in the AA (anti-anti) conformation</th>
<th>butyl group in the GA (gauche-anti) conformation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Approximate Description</td>
<td>Approximate Description</td>
</tr>
<tr>
<td>1</td>
<td>30.4 N-C7 tor</td>
<td>27.5 N-C7 tor</td>
</tr>
<tr>
<td>2</td>
<td>58.3 N-C6 tor</td>
<td>58.3 N-C6 tor</td>
</tr>
<tr>
<td>3</td>
<td>74.3 C7-C8 tor</td>
<td>76.6 N-C6 tor + C7-C8 tor</td>
</tr>
<tr>
<td>4</td>
<td>81.8 N-C6 tor + N-C7-C8 bend</td>
<td>82.5 C7-C8 tor</td>
</tr>
<tr>
<td>5</td>
<td>116.5 N-C7 tor</td>
<td>156.7 N-C6 oopl bend + C8H₂ rock</td>
</tr>
<tr>
<td>6</td>
<td>203.6 chain def + N-C6 oopl bend</td>
<td>205.1 chain def + N-C6 oopl bend</td>
</tr>
<tr>
<td>7</td>
<td>250.9 N-C6 + N-C7H₂ oopl ooph bend</td>
<td>251.1 N-C6 + N-C7H₂ oopl ooph bend</td>
</tr>
<tr>
<td>8</td>
<td>252.8 C9-C10 tor</td>
<td>258.4 C9-C10 tor</td>
</tr>
<tr>
<td>9</td>
<td>278.8 C7H₂ rock + C6H₃ iph bend</td>
<td>296.1 C7H₂ rock + C6H₃ iph bend</td>
</tr>
<tr>
<td>10</td>
<td>327.1 ring wag + chain def</td>
<td>333.3 ring wag + chain def</td>
</tr>
<tr>
<td>11</td>
<td>407.0 ring rot + C7H₂ rock + C6H₁ rock</td>
<td>418.0 ring rot + C7H₂ rock + N-C6H₃ iph rock</td>
</tr>
<tr>
<td>12</td>
<td>441.0 N-C7 oopl bend + N-C6 oopl ooph bend + chain bend + CH₂ wag + ring rot</td>
<td>503.7 N-C7 oopl bend + N-C7-C8-C9 angles bend</td>
</tr>
<tr>
<td>13</td>
<td>619.6 ring oopl def + C7H₂ rock + C7-C8-C9 bend</td>
<td>603.9 N-C6 N-C7 iph str + ring oopl def + C8H₂ rock + N-C7-C8 bend.</td>
</tr>
<tr>
<td>14</td>
<td>636.2 ring def (C2-H oopl bend) + N-C6 N-C7 iph str + C7H₂ rock + C7-C8-C9 bend</td>
<td>622.8 ring def (C2-H C4-H iph oopl bend) + C8H₂ rock + N-C7-C8 bend.</td>
</tr>
<tr>
<td>15</td>
<td>670.2 N-C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H₂ wag + N-C7-C8 bend</td>
<td>662.8 ring def (bend around line NN) + C8H₂ rock + N-C7-C8 bend</td>
</tr>
<tr>
<td>16</td>
<td>725.5 Ring C-H oopl bend (bend around NN line)</td>
<td>712.8 N-C₆ N-C7 oophil str + ring iph def + C8H₂ rock + C7-C8 tor</td>
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<td>17</td>
<td>748.8 N-C6 N-C7 oophil str + ring spl def + N-C7-C8 and C7-C8-C9 bend</td>
<td>725.1 Ring C-H oopl bend (bend around NN line)</td>
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<td>18</td>
<td>754.6 chain CH₃ sci + rock</td>
<td>773.5 Chain CH₃ rock + ring C-H oophil iph bend (umbrella)</td>
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<tr>
<td>19</td>
<td>791.7 ring C-H oophil iph bend (umbrella)</td>
<td>790.4 ring C-H oophil iph bend (umbrella)</td>
</tr>
<tr>
<td>20</td>
<td>813.7 C₄-H C₅-H oophil oophil bend (twi)</td>
<td>811.5 C₄-H C₅-H oophil oophil bend (twi)</td>
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<tr>
<td>21</td>
<td>819.3 chain CH₃ sci</td>
<td>853.9 Chain CH₃ sci</td>
</tr>
<tr>
<td>22</td>
<td>945.3 chain def + C10H₂ rock</td>
<td>912.4 Chain def + C10H₂ rock</td>
</tr>
<tr>
<td>23</td>
<td>969.8 chain def (CH₂ twi + rock)</td>
<td>981.5 Chain def (CH₂ sci + rock)</td>
</tr>
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<td>24</td>
<td>1043.6 ring def + chain def</td>
<td>1025.7 ring def + chain def</td>
</tr>
<tr>
<td>25</td>
<td>1057.3 ring def + N-C6 str + C₄-H C₅-H iph iph bend</td>
<td>1051.9 ring def + N-C6 str + N-C7 str + C7-C8 str</td>
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<td></td>
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<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>26</td>
<td>1070.3</td>
<td>C4-H ipb bend + C7-C8 str</td>
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<tr>
<td>27</td>
<td>1106.6</td>
<td>chain def</td>
</tr>
<tr>
<td>28</td>
<td>1128.4</td>
<td>C6H2 ipb rock + ring def</td>
</tr>
<tr>
<td>29</td>
<td>1149.9</td>
<td>C4-H C5-H ipb bend (sci)</td>
</tr>
<tr>
<td>30</td>
<td>1167.0</td>
<td>chain def (C-C str)</td>
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<td>31</td>
<td>1176.9</td>
<td>C6H2 def (oopl rock)</td>
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<tr>
<td>32</td>
<td>1182.7</td>
<td>C2-H ipb bend, C6H2 def, chain CH3 def</td>
</tr>
<tr>
<td>33</td>
<td>1212.3</td>
<td>C6-N C7-N oopl str + ring C-H ipb bend</td>
</tr>
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<td>34</td>
<td>1272.5</td>
<td>ring CH iph ipb bend + chain CH2 def</td>
</tr>
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<td>35</td>
<td>1318.4</td>
<td>ring CH iph ipb bend + chain CH2 wag</td>
</tr>
<tr>
<td>36</td>
<td>1324.3</td>
<td>ring CH iph ipb bend + chain CH2 def</td>
</tr>
<tr>
<td>37</td>
<td>1353.0</td>
<td>chain CH2 def + ring CH iph ipb bend</td>
</tr>
<tr>
<td>38</td>
<td>1371.8</td>
<td>C8H2 C9H2 twi</td>
</tr>
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<td>1388.9</td>
<td>ring breathing + C7H2 twi</td>
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<tr>
<td>40</td>
<td>1413.6</td>
<td>C7H2 C9H2 wag</td>
</tr>
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<td>41</td>
<td>1443.7</td>
<td>chain CH2 wag</td>
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<tr>
<td>42</td>
<td>1450.6</td>
<td>ring asym str + C7H2 twi + C6H2 def</td>
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<td>1472.7</td>
<td>C10H2 def (umbrella)</td>
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<td>44</td>
<td>1490.9</td>
<td>ring asym str + C6H2 def (umbrella)</td>
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<td>45</td>
<td>1505.4</td>
<td>C6H2 def (umbrella)</td>
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<td>46</td>
<td>1534.6</td>
<td>C6H2 def</td>
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<td>47</td>
<td>1539.1</td>
<td>C7H2 + C8H2 bend (sci)</td>
</tr>
<tr>
<td>48</td>
<td>1545.1</td>
<td>chain CH3 bend (sci)</td>
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<tr>
<td>49</td>
<td>1554.8</td>
<td>C7H2 + C8H2 + C10H2 bend (sci)</td>
</tr>
<tr>
<td>50</td>
<td>1559.8</td>
<td>C10H2 def</td>
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<td>51</td>
<td>1562.7</td>
<td>C6H2 def</td>
</tr>
<tr>
<td>52</td>
<td>1566.6</td>
<td>chain CH2 bend (sci)</td>
</tr>
<tr>
<td>53</td>
<td>1620.5</td>
<td>C4-C5 ring str + C4-H + C5-H ipb sym bend</td>
</tr>
<tr>
<td>54</td>
<td>1645.7</td>
<td>C2-N ring asym str + C2-H ipb bend</td>
</tr>
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<td>3120.7</td>
<td>C8H2 + C9H2 iph str (sym)</td>
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<td>56</td>
<td>3128.6</td>
<td>C8H2 + C9H2 ooph str (sym)</td>
</tr>
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<td>57</td>
<td>3135.6</td>
<td>C10H2 iph str (sym)</td>
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<td>3160.9</td>
<td>C7H2 iph str (sym)</td>
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<td>59</td>
<td>3164.3</td>
<td>C6H2 iph str (sym)</td>
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<td>C8H2 + C9H2 ooph str (asym)</td>
</tr>
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<td>61</td>
<td>3190.6</td>
<td>C8H2 + C9H2 ooph str (asym)</td>
</tr>
<tr>
<td>62</td>
<td>3229.5</td>
<td>C10H2 ooph str (asym)</td>
</tr>
<tr>
<td>63</td>
<td>3232.0</td>
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</tr>
<tr>
<td>64</td>
<td>3240.4</td>
<td>C10H2 ooph str (sym)</td>
</tr>
<tr>
<td>65</td>
<td>3278.6</td>
<td>C6H2 ooph str (sym)</td>
</tr>
<tr>
<td>#</td>
<td>cm⁻¹</td>
<td>Description</td>
</tr>
<tr>
<td>----</td>
<td>-------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>66</td>
<td>3286.3</td>
<td>C₆H₃ ooph str (sym)</td>
</tr>
<tr>
<td>67</td>
<td>3359.7</td>
<td>C₃-H C₄-H ooph str (asym)</td>
</tr>
<tr>
<td>68</td>
<td>3363.0</td>
<td>C₂-H str</td>
</tr>
<tr>
<td>69</td>
<td>3377.4</td>
<td>C₃-H C₄-H iph str (sym)</td>
</tr>
</tbody>
</table>

*Key of approximate group vibrations: asym = asymmetric, bend = angle bending (scissoring), breathing = all ring bonds iph, def = more complicated deformation of skeleton, ipl = in plane, iph = in phase (symmetric), oopl = out of ring plane, ooph = opposite motion, out of phase (asymmetric), ring = imidazole core, rot = ring rotation, as a wheel, with carbon H atoms, rock = rocking (like V to V by rotation around an axis out of the paper), sci = non-connected scissoring, str = bond stretching, sym = symmetric, tor = torsion around specified bond, twi = twisting of CH₂ group or chain, wag = wagging (like V to v by rotation around an axis in the paper, →).
Table 2. Experimentally observed Raman spectral bands for two common [C₄C₁Im]⁺ ionic liquids, given in cm⁻¹, and approximate assignments.

<table>
<thead>
<tr>
<th>ν /cm⁻¹</th>
<th>Assignments*</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄C₁Im] [PF₆]</td>
<td>[C₄C₁Im] [BF₄]</td>
</tr>
<tr>
<td>498</td>
<td>500 N-C7 opl bend + N-C7-C8-C9 angles bend (GA12)</td>
</tr>
<tr>
<td>568</td>
<td>ν₂(PF₆) stretching</td>
</tr>
<tr>
<td>601</td>
<td>601 N-C6 N-C7 iph str + ring oopl def + C8H₂ rock + N-C7-C8 bend. (GA13)</td>
</tr>
<tr>
<td>624</td>
<td>625 ring def (C2-H oopl bend) + N-C6 N-C7 iph str + C7H₂ rock + C7-C8-C9 bend (AA14)</td>
</tr>
<tr>
<td>656</td>
<td>658 N-C6 str + ring def (N1 and H on C2 oopl oopf departure) + C8H₂ wag + N-C7-C8 bend (AA15) + ring def (bend around line NN) + C8H₂ rock + N-C7-C8 bend (GA15)</td>
</tr>
<tr>
<td>698</td>
<td>699 N-C6 N-C7 ooph str + ring ipl def + C8H₂ rock + C7-C8 tor (GA16)</td>
</tr>
<tr>
<td>730 hidden ? ∼735 N-C6 N-C7 ooph str + ring ipl def + N-C7-C8 and C7-C8-C9 bend (AA17)</td>
<td></td>
</tr>
<tr>
<td>741</td>
<td>ν₁(PF₆) stretching</td>
</tr>
</tbody>
</table>

*Key for descriptions of approximate group vibrations, see Table 1; AA and GA mode numbers given in parentheses.
Table 3. Selected vibrational modes as determined in MP2 calculations for the [C₄C₁Im]⁺ cation in AA and GA conformation. Given are the predicted wavenumber, relative IR and Raman intensities as well as descriptions of the selected modes {46}.

<table>
<thead>
<tr>
<th>Mode</th>
<th>ν/ cm⁻¹</th>
<th>IR intensity / km mole⁻¹</th>
<th>Raman activity / Å⁴ amu⁻¹</th>
<th>Approx. Description*</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[C₄C₁Im]⁺ cation in AA conformation</td>
</tr>
<tr>
<td>13</td>
<td>620</td>
<td>0.52</td>
<td>1.34</td>
<td>ring oopl def + C7H₂ rock + C7-C8-C9 bend</td>
</tr>
<tr>
<td>14</td>
<td>636</td>
<td>9.40</td>
<td>2.59</td>
<td>ring def (C2-H oopl bend) + N-C6 N-C7 iph str + C7H₂ rock + C7-C8-C9 bend</td>
</tr>
<tr>
<td>15</td>
<td>670</td>
<td>12.23</td>
<td>1.36</td>
<td>N-C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H₂ wag + N-C7-C8 bend</td>
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<tr>
<td>17</td>
<td>749</td>
<td>13.06</td>
<td>2.13</td>
<td>N-C6 N-C7 ooph str + ring ipl def + N-C7-C8 and C7-C8-C9 bend</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[C₄C₁Im]⁺ cation in GA conformation</td>
</tr>
<tr>
<td>12</td>
<td>504</td>
<td>0.65</td>
<td>1.19</td>
<td>N-C7 opl bend + N-C7-C8-C9 angles bend</td>
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<td>1.46</td>
<td>5.99</td>
<td>ring ipl def + C8H₂ rock + N-C7-C8 bend</td>
</tr>
<tr>
<td>14</td>
<td>623</td>
<td>2.82</td>
<td>0.36</td>
<td>ring def (C2-H C4-H iph oopl bend) + C8H₂ rock + N-C7-C8 bend</td>
</tr>
<tr>
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<td>663</td>
<td>15.62</td>
<td>0.56</td>
<td>ring def (bend around line NN) + C8H₂ rock + N-C7-C8 bend</td>
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<tr>
<td>16</td>
<td>713</td>
<td>6.65</td>
<td>2.15</td>
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N-C₆ N-C₇ ooph str + ring ipl def + C₈H₂ rock + C₇-C₈ tor

* For key of approximate group vibrations, see Table 1.
Figure 1. Common ionic liquids include ammonium, phosphonium, sulfonium, guanidinium, pyridinium, imidazolium, and pyrrolidinium cations and $\text{Cl}^-$, $\text{Br}^-$, $\text{BF}_4^-$, $\text{PF}_6^-$, $\text{TfO}^-$ (trifluoromethane-sulfonate) and $\text{[Tf}_2\text{N}]^-$ (bis(trifluoromethylsulfonyl)imide) anions. However, use of nomenclature vary among researchers. We prefer the notation $[\text{C}_4\text{C}_1\text{Im}]^+$ for 1-butyl-3-methylimidazolium instead of $[\text{bmim}]^+$, $[\text{BMIM}]^+$ or others. Similarly, e.g. we will call the bis(trifluoromethanesulfonyl)imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ anion $[\text{Tf}_2\text{N}]^-$ (Tf is a short-hand notation for triflate); other acceptable abbreviated names occur in recent literature.
Figure 2. Numbering scheme in the 1-hexyl-3-methylimidazolium cation, \([\text{C}_6\text{C}_1\text{Im}]^+\), showing the three ring protons H2, H4, and H5.
Figure 3. The relationships between infrared absorption, Rayleigh and Raman scattering:
Figure 4. Crystal structure of [C₄C₁Im]Cl "Crystal (1)" viewed along the $a$ axis. Only carbon atoms, nitrogen atoms, and chloride anions are shown. The \textit{anti-anti} (AA) conformation of the [C₄C₁Im]$^+$ cation is shown in the inset. The butyl group C-C bonds are shown as thick bars. Note that the cations and chloride anions form characteristic columns along the crystal $a$ axis (figure adapted from Hamaguchi et al. \cite{50}).
Figure 5. Crystal structure of [C₄C₇Im]Br viewed in the direction of the $a$ axis. Only carbon atoms, nitrogen atoms, and bromide anions are shown. The gauche-anti (GA) conformation of the [C₄C₇Im]$^+$ cation is shown in the inset. The butyl group C-C bonds are shown as thick bars (figure adapted from Hamaguchi et al. {50}).
Figure 6. Raman spectra of (a) [C$_4$C$_1$Im]Cl "Crystal (1)", (b) [C$_4$C$_1$Im]Cl "Crystal (2)", and (c) [C$_4$C$_1$Im]Br crystals. (a) differs from (b) and (c) (figure has been adapted from Hamaguchi et al. {50}).
Figure 7. Raman spectra of liquid [C₄C₁Im]X, where X = Cl (a), Br (b), I (c), [BF₄] (d), and [PF₆] (e). The anion bands in (d) and (e) have been deleted (50). Spectra of [C₄C₁Im]Cl "Crystal (1)" and crystalline [C₄C₁Im]Br, respectively, are included as (f) and (g), for reference purposes (figure adapted from Hamaguchi et al. (50)).
Figure 8. Optimized structures of the $[\text{C}_4\text{C}_1\text{Im}]^+$ cation in the two crystals. Experimental (continuous lines) and calculated Raman spectra (solid vertical bars) of $[\text{C}_4\text{C}_1\text{Im}]\text{Cl}$ "Crystal (1)" (above) and $[\text{C}_4\text{C}_1\text{Im}]\text{Br}$ (below) are shown (figure has been adapted from Hamaguchi et al. {50}, {70}).
Figure 9. Calculated normal modes of key bands of the AA and GA forms of the [C₄C₁Im]⁺ cation. The arrows indicate vibrational amplitudes of atoms. The C8 methylene group is surrounded by a circle. Obviously it appears that the CH₂ rocking vibration is coupled to the ring modes only for the GA conformer, thereby lowering the frequencies. Graphics adapted from Hamaguchi et al. {50}. 
Figure 10. Calculated Raman spectra of two conformers of the $[\text{C}_4\text{C}_1\text{Im}]^+$ cation in the range between 3400 and 2900 cm$^{-1}$. a: The anti-anti conformer; b: The gauche-anti conformer. Data from {72}.
Figure 11. Calculated Raman spectra of two conformers of the $[\text{C}_{4}\text{C}_{1}\text{Im}]^+$ cation in the range between 1650 and 400 cm$^{-1}$. a: The \textit{anti-anti} conformer; b: The \textit{gauche-anti} conformer. Data from {46} and {72}.
Figure 12. Some of our calculated normal modes of certain bands of the AA and GA forms of the $[\text{C}_4\text{C}_1\text{Im}]^+$ cation. The arrows indicate vibrational amplitudes of atoms. As found by Hamaguchi et al. \cite{50} also our C8 methylene CH$_2$ rocking vibration was coupled to the ring modes only for the gauche-anti conformer \cite{46} and \cite{72}. 
Figure 13. Details of FT-Raman spectra of the [C$_4$C$_1$Im][PF$_6$] and [C$_4$C$_1$Im][BF$_4$] ionic liquids at ∼25ºC {72}. Note that the characteristic bands of the AA and GA forms of the [C$_4$C$_1$Im]$^+$ cation are present in both melts, as also found e.g. by Hamaguchi et al. {50}. 
Figure 14. Minimized molecular structure of [C₄CⁱIm][PF₆] (B3LYP/6-31G*) {5}. Found hydrogen bonds included: F2-H25 = 2.279 Å; F2-H18 = 2.042 Å; F1-H18 = 2.441 Å; F5-H18 = 2.070 Å, F5-H22 = 2.419 Å and F1-H26 = 2.377 Å. Figure adapted from Meng et al. {5}. 
Figure 15. Calculated structures of the [C\text{2C1Im}]^+ cation, showing the two different torsion conformers obtainable by rotation of the ethyl group around the C-N bond relative to the imidazolium ring. Planar (left) and nonplanar (right) rotamers are viewed perpendicular to and along the ring plane. The nonplanar form is known from X-ray structures \{69\}. Figure adopted from Umebayashi et al. \{80\}. 
Figure 16. FT-Raman spectra of the [C₆C₄Im][PF₆] and [C₄C₄Im][PF₆] ionic liquids at ~25ºC. Note that the characteristic bands of the AA and GA forms of the [C₄C₄Im]+ cation are very much like the AAAA and GAAA bands from the [C₆C₄Im]+ cation \{46\} \{72\}. 
Figure 17. Our calculated Raman spectra of two conformers of the hexyl [C₆C₇Im]⁺ cation between 750 and 500 cm⁻¹. a: all-anti conformer AAAA; b: gauche-anti-anti-anti GAAA conformer {46}.
Figure 18. Raman spectra of 1-alkyl-3-methylimidazolium tetrafluoroborate liquids, [CₙC₃Im][BF₄] for n = 10, 8, 7, 6, 5, 4, 3, and 2. The figure has been adapted from Hamaguchi et al. {50}.
Figure 19. Time-resolved Raman spectra of the melting and thermal equilibration process at 72°C for a [C₄C₁Im]Cl “Crystal (1)” sample. The figure has been adapted from Hamaguchi et al. {50}, {86}.
Figure 20. Conceptual structure of ionic salt crystals and liquids: a = crystal, b and c = liquid crystals, d = liquid, e = ionic liquid, according to the model of Hamaguchi and Ozawa {50}. Figure adapted from Hamaguchi et al. {50}.
Figure 21. Raman spectra of the 1-ethyl-3-methylimidazolium liquid \([\text{C}_2\text{C}_1\text{Im}][\text{ Tf}_2\text{N}]\) showing the temperature dependent \(\text{SO}_2\) wagging bands at \(~\text{398 and 407 cm}^{-1}\). According to Fujii et al. \{108\} the bands arise from different conformers of the [Tf₂N]⁻ ion, known also from crystal structures \{109\}. Figure adapted from Fujii et al. \{108\}.
Figure 22. Different conformers of symmetry $C_1$ and $C_2$ of the [Tf$_2$N]$^-$ ion, as determined by Fujii et al. \cite{108} by means of DFT calculations for the 1-ethyl-3-methylimidazolium liquid [C$_2$C$_1$Im][Tf$_2$N]. Figure adapted from Fujii et al. \cite{108}.
Figure 23. Our Raman spectrum of liquid [C₄C₃Im][Tf₂N]. Apparently the splitting between the two conformation sensitive bands for the [Tf₂N]⁻ ion, near ~400 cm⁻¹, is not so large in this liquid as for the 1-ethyl [C₂C₃Im][Tf₂N] case {108}. The CF₃ symmetric stretching and deformation bands are seen at 1242 and 742 cm⁻¹. The AA/GA conformational equilibrium bands at 500-700 cm⁻¹ discussed in relation with Fig. 7 can also be weakly seen {72}.
Figure 24. Structure and conformations of N-butyl-N-methylpyrrolidinium (or 1-butyl-1-methylpyrrolidinium or [P14]+ or [bmpy]+; several names are used). In [P14]+ P denotes pyrrolidinium and the digits the number of carbon atoms in radicals R<sup>1</sup> and R<sup>2</sup>. Also, the ion is commonly called [bmpy]+ (N is atom number 1). The ring of the (CH<sub>2</sub>)<sub>4</sub>NR<sup>1</sup>R<sup>2</sup> pyrimidinium ion is not planar and has two stable (twist and envelope) forms.
Figure 25. Experimental FT-Raman spectra for the [bmpy][Tf₂N] liquid (also called [P14][TFSI] {113}), showing that the spectrum (top) at room temperature essentially consists of bands from both the [Tf₂N]⁻ anion (middle) and the [bmpy]⁺ cation (bottom) (shifted conveniently). The Li⁺ and Cl⁻ do not contribute bands directly in the liquid but have influence on the structures of the salts and are interacting with the ions and influencing the conformational equilibria in the IL {72}. 
Figure 26. Minimized structures of the so-called *ax-envelope:trans-TT* and *-TG* conformations of the [bmpy]$^+$ ion in assumed gaseous state calculated \(^{72}\) at the DFT/B3LYP/6-31+G (p,d) level. The minimized bond distances and angles had standard magnitudes. The model spectra shown compare well to the experimental FT-Raman spectrum of the [bmpy]$^+$ ion in the solid chloride salt \(^{72}\).
Figure 27. Illustrative example of the power of *ab-initio* methods combined with Raman spectroscopy, applied on the [TMGH][Tf₂N] liquid. The two top spectral curves show calculated Raman spectra of minimized conformers of [Tf₂N]⁻ and [TMGH]⁺ at the DFT/B3LYP/6-31G(d) level. The geometries of
the ions are also depicted together with the sum of the spectra, constituting a hypothetical [TMGH][Tf$_2$N] liquid of non-interacting ions (shifted conveniently). Bottom: the experimental FT-Raman spectrum. Unfortunately measurements exist only below 3500 cm$^{-1}$ \cite{72}.