Vibrational Spectroscopy of Ionic Liquids

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Supporting Information

ABSTRACT: Vibrational spectroscopy has continued use as a powerful tool to characterize ionic liquids since the literature on room temperature molten salts experienced the rapid increase in number of publications in the 1990’s. In the past years, infrared (IR) and Raman spectroscopies have provided insights on ionic interactions and the resulting liquid structure in ionic liquids. A large body of information is now available concerning vibrational spectra of ionic liquids made of many different combinations of anions and cations, but reviews on this literature are scarce. This review is an attempt at filling this gap. Some basic care needed while recording IR or Raman spectra of ionic liquids is explained. We have reviewed the conceptual basis of theoretical frameworks which have been used to interpret vibrational spectra of ionic liquids, helping the reader to distinguish the scope of application of different methods of calculation. Vibrational frequencies observed in IR and Raman spectra of ionic liquids based on different anions and cations are discussed and eventual disagreements between different sources are critically reviewed. The aim is that the reader can use this information while assigning vibrational spectra of an ionic liquid containing another particular combination of anions and cations. Different applications of IR and Raman spectroscopies are given for both pure ionic liquids and solutions. Further issues addressed in this review are the intermolecular vibrations that are more directly probed by the low-frequency range of IR and Raman spectra and the applications of vibrational spectroscopy in studying phase transitions of ionic liquids.

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1. INTRODUCTION

Vibrational and NMR spectroscopies are fundamental tools to characterize ionic liquids. The vibrational spectroscopy techniques of infrared (IR) and Raman permeate the literature on essentially all of the actual or potential applications envisaged for ionic liquids. IR and Raman spectroscopies have provided deep insights on the nature of ionic interactions, the role played by anion–cation hydrogen bonds, molecular conformations, and their modifications as pressure and temperature is varied in the normal liquid phase, during phase transition to crystalline or amorphous (glassy) solid phases, after vaporization, etc. The user of a vibrational spectroscopy technique needs to have in hand reliable interpretation of vibrational spectra, in particular, assignment of experimental frequencies to vibrational motions of the common ions of ionic liquids. This information is usually not available.
available from studies which are more dedicated to theoretical and computational issues related to vibrational spectroscopy. Quantum chemistry methods are now routinely used to calculate vibrational frequencies to be compared to experimental data. However, strong ionic interactions may imply that comparison between experimental and calculated frequencies by a relatively fast ab initio calculation is far from straightforward. In fact, scrutinizing the large body of literature on vibrational spectroscopy of ionic liquids, eventually there is no full agreement between different authors for the same system. Other schemes have been considered for assigning vibrational spectra of ionic liquids (e.g., taking advantage of molecular dynamics simulations of liquids). On the other hand, even though vibrational spectroscopy has a long history in studying high temperature molten salts and some ions are common species for both high and room temperature molten salts (e.g., relatively simple polyatomic anions), sometimes previous knowledge on vibrational spectroscopy of molten salts is not fully appreciated within the context of ionic liquids. Moreover, vibrational spectroscopy is well appropriate for studying intermolecular interactions not only in pure ionic liquids but also in ionic liquids mixtures, solutions of molecular or ionic solutes in ionic liquids, gas absorption, etc.

This review addresses the above-mentioned issues and others, aiming to be useful for users who employ IR and Raman spectroscopies combined with other techniques while investigating ionic liquids and also for those who are involved in assignments of vibrational spectra of ionic liquids. Papatheodorou et al. published important reviews on Raman spectroscopy of high temperature molten salts, but previous reviews on vibrational spectroscopy of ionic liquids are scarce. In 2007, Berg published a review on Raman spectroscopy and ab initio calculations of ionic liquids. Berg’s review focused on the spectroscopic signatures of molecular conformations achieved by the ions, mainly 1-alkyl-3-methylimidazolium and N,N-dialkylypyrrolidinium cations, and the bis(trifluoromethanesulfonyl)imide anion, [NTf2]. These Raman spectroscopic studies have been reviewed more recently by Saha et al. The more specific issue of vibrational spectroscopy of ionic liquid surfaces using linear and nonlinear techniques has also been reviewed recently. In this review, we will address both IR and Raman studies encompassing a wide group of cations and anions commonly used in forming ionic liquids. Figure 1 shows molecular structures of several cations and anions whose vibrational spectra will be discussed in this review, together with notation used throughout this work.

This review addresses many issues in which vibrational spectroscopy has given fundamental contributions for our current understanding about interactions and structure of ionic liquids along the last two decades. The review focuses on linear IR and Raman spectroscopies, being beyond the scope of techniques such as time-resolved IR spectroscopy and coherent anti-Stokes Raman scattering (CARS) which have recently been applied for investigating ionic liquids. On the other hand, we will address far-infrared (FIR) and low-frequency Raman spectroscopy studies of ionic liquids. Thus, results obtained from optical Kerr effect (OKE) spectroscopy, being the counterpart of low-frequency Raman spectroscopy, will be mentioned, even though OKE is a time-resolved spectroscopy technique, because it has been the most common technique probing the low-frequency vibrations of ionic liquids.

The review is organized as follows. We provide experimental details in section 2 since most of spectra shown below have been especially obtained for the purpose of this review. Raman spectroscopy of high temperature molten salts demand nontrivial experimental skills for building furnaces and sample containers for handling corrosive and air-sensitive melts. In contrast, IR and Raman measurements of ionic liquids are more easily carried out since the liquid sample may be simply accommodated in quartz tubes. Nevertheless, some warnings on the experimental side are timely. All of IR and Raman spectra recorded in this work are available for the reader in TXT files. The usefulness of vibrational spectroscopy is heavily linked to the calculation of vibrational frequencies, so that section 3 reviews the methods which have been applied for calculating vibrational spectra of ionic liquids. These methods include classical normal coordinate analysis, ab initio calculation for an isolated ion or for a cluster of ions, and classical or ab initio molecular dynamics simulations of liquids. The scope of section 3 is not technical details of all of these methods; instead, the section focuses on the conceptual basis of them, helping the reader to distinguish the assumptions and the need for different methods of calculation. Section 4 reviews vibrational spectroscopy studies of pure ionic liquids, being the longest section of this work. This section discusses the assignment of vibrational frequencies of the most common anions (section 4.1) and cations (section 4.2) which form ionic liquids. These two sections are already plenty of applications of vibrational spectroscopy in studying pure ionic liquids, but further applications are given in section 4.3. It is our hope that the vibrational assignments discussed thoroughly in this section helps the reader to interpret vibrational spectra when working with a given ionic liquid based on a different combination of anions and cations. We separated in section 5 the discussion of the low-frequency range, as this range directly manifests the liquid structure and intermolecular dynamics of ionic liquids.

Studies concerning the low-frequency range of vibrational spectra of ionic liquids have been developed along two different research lines, one by workers using far-infrared (FIR) and other by workers using low-frequency Raman spectroscopy, in
particular OKE spectroscopy. Section 5 is an attempt at putting into a proper perspective the results from FIR and low-frequency Raman spectroscopy that have been obtained along the past decade. The accumulated knowledge on the nature of vibrational motions and characteristic frequencies in the normal liquid phase discussed in sections 4 and 5 is then applied in section 6 for studying phase transitions, in particular crystallization and glass transition experienced by ionic liquids under low temperature or high pressure. In section 7, we move to ionic liquids solutions. Since ionic liquids as solvents encompass a very large range of applications, from gas molecules to cellulose, and in each of these areas vibrational spectroscopy has given its contribution, section 7 gives some representative examples of the capability of vibrational spectroscopy in shedding light on solute–ionic liquid interactions. Section 8 closes the review with some concluding remarks.

2. EXPERIMENTAL DETAILS

IR and Raman spectra of several ionic liquids were recorded for specific purposes of this review. The spectra are available as TXT files. The ionic liquids used in this work were purchased from different suppliers (e.g., Iolitec, Solvionic, Aldrich, and Merck). Most of the purchased ionic liquids have purity superior to 98%, and they were used without further purification except for the drying process as discussed below.

Fourier transform IR spectra were recorded with a Bruker Alpha equipment with a DTGS detector and KBr optics. IR spectra measured by transmission were obtained from thin films of liquid samples between KRS-5 windows. In the case of solid samples, we used the attenuated total reflection (ATR) Platinum accessory (Bruker) with diamond crystal and a single reflection. Spectral resolution was 2 cm\(^{-1}\). Optical effects can result in differences between transmission and reflection measurements. ATR is a technique appropriate for quantitative IR spectroscopy since it allows for better control of sample size and thickness. Moreover, ATR Fourier transform IR spectrum can be used to obtain optical constants (i.e., frequency-dependent refractive index and extinction coefficient), as shown by Buffeteau et al. for different ionic liquids. Figure 2 illustrates differences in relative intensities and vibrational frequencies that can be found between transmission and ATR measurements of IR spectra of a given ionic liquid, [C\(_4\)C\(_1\)im][CF\(_3\)SO\(_3\)]. A combination of transmission and ATR infrared spectroscopy has been used by Burba et al. as a methodology to infer about charge organization in the series [C\(_n\)C\(_1\)im][CF\(_3\)SO\(_3\)], n = 2–8. They considered the intense IR band of the anion symmetric stretching mode, \(\nu_{\text{sym}}(\text{SO}_3^-)\), with maximum at 1031 cm\(^{-1}\). The approach is based on a first estimate of the dipole moment derivative from a transmission measurement according to the dipolar coupling theory, which assumes a quasilattice organization of the ions. A second estimate of the dipole moment derivative is obtained from optical constants obtained from an ATR measurement, which is not based on the quasilattice model. The ratio between these two values of dipole moment derivatives indicates the degree of quasilattice structure in the ionic liquid. Burba et al. showed that such charge ordering decreases with increasing length of the alkyl chain in [C\(_n\)C\(_1\)im][CF\(_3\)SO\(_3\)]. It should be noted, however, that the method also relies on assigning the asymmetric shape of the \(\nu_{\text{as}}(\text{SO}_3^-)\) IR band as the result of longitudinal optic–transverse optic (LO-TO) splitting to be considered within the dipolar coupling theory. All of the IR spectra recorded in this work will be reported in transmittance, except Figures 2 and 5 where IR spectra are shown in absorbance.

Raman spectra were obtained with a Horiba-Jobin-Yvon T64000 triple monochromator spectrometer equipped with a Coherent laser, typically with 200 mW of output power. Suitable to reduce the Rayleigh scattering line, is particularly important for the low-frequency range, \(S < \omega < 100 \text{ cm}^{-1}\), to be discussed in section 5. Raman spectra were obtained in 180° scattering geometry. There was no selection of polarization of scattered light for most of the Raman spectra shown in this review, otherwise some polarized and depolarized Raman spectra will be shown as mentioned in text. The excitation line used was the 647.1 nm line of a mixed argon–krypton Coherent laser, typically with 200 mW of output power. Fluorescence background is a known issue in Raman spectroscopy of (high temperature) molten salts. Even though most ionic liquids are colorless, we use a red laser line to excite Raman spectra in order to reduce eventual fluorescence background. For instance, Figure 3 shows Raman spectra obtained with excitations at 514.5 and 647.1 nm for the same sample of a colorless ionic liquid, [C\(_n\)C\(_1\)im][PF\(_6\)]. The same laser power was used to obtain the spectra of Figure 3, and no baseline correction was done, so that it is clear that fluorescence background is strongly reduced when using the 647.1 nm laser line. Whenever fluorescence precluded obtaining suitable...
A relatively stringent spectral resolution is eventually required since the complex molecular structures of the ions result in overlapping of bands. Figure 4 illustrates the effect of spectral resolution in the Raman spectrum of [C₄C₁im][NTf₂] within the spectral range of the anion SO₂ wagging mode. This figure exhibits a single broad band at ~400 cm⁻¹ when using poor spectral resolution, but the band is resolved into two peaks at 397 and 404 cm⁻¹ when using better spectral resolution. In this work, Raman spectra were obtained with spectral resolution of 2 cm⁻¹, taking into consideration compromise on good signal-to-noise ratio.

All the samples used in this work were submitted to a drying process under high vacuum (10⁻⁵ mbar) at ~60 °C for 48 h prior the analysis. The samples were then manipulated inside a drybox with argon atmosphere. It has been shown that small amount of water can have significant effect on ionic liquids properties.²⁵⁻²⁸ Karl Fischer coulometric titration is the usual method to quantify water, but IR spectroscopy has been applied to measure water content in ionic liquids. Andanson et al.²⁷ used the O–H stretching mode of water in the range 3400–3800 cm⁻¹, and Fadeeva et al.²⁸ used a combination band of water at ~5250 cm⁻¹ to measure the water content in ionic liquids. Cammarata et al.²⁹ showed by using IR spectroscopy that interactions between water and the ions are dominated by anion–water interactions in the case of nonprotic ionic liquids based on imidazolium cations. In the case of a mixture of 919 liquids, it is worth noting that accurate analysis of band intensity should take into account the fact that the effective path length eventually changes in ATR-IR measurements because the refractive index of the sample depends on the concentration of the solution.³⁰ Figure 5 illustrates the evolution of the drying process as monitored by IR spectroscopy for three ionic liquids with the same [C₄C₁im]⁺ cation but anions with distinct coordination strength or basicity, [NTf₂]⁻, [CF₃SO₃]⁻, and [CH₃COO]⁻. The Karl Fischer analyses of [C₄C₁im][NTf₂], [C₄C₁im][CF₃SO₃], and [C₄C₁im][CH₃COO] indicated water concentration of 284, 835, and 22353 ppm, respectively, for the samples as taken straight from their flask prior to any drying attempt. Water content dropped to 214, 298, and 18795 ppm after 48 h under high-vacuum at room temperature, and when the sample was simultaneously warmed to ~60 °C, the water content achieved 45, 118, and 8580 ppm, respectively. This trend is manifested in the IR spectra of Figure 5 by the comparison between relative intensities of water bands (3400–3800 cm⁻¹) and ionic liquid bands (2800–3200 cm⁻¹).

The drying protocol using high vacuum at room temperature seems enough for a less viscous ionic liquid and less

Figure 4. Raman spectra of [C₄C₁im][NTf₂] in the range of SO₂ wagging mode recorded with different spectrometer resolutions. Raman spectrum obtained with 0.5 cm⁻¹ of spectral resolution is shown with the intensity multiplied by a factor of 20.

Figure 5. IR spectra of (A) [C₄C₁im][NTf₂], (B) [C₄C₁im][CF₃SO₃], and (C) [C₄C₁im][CH₃COO] before and after the drying processes showing the spectral range of water bands (3400–3800 cm⁻¹). The asterisk in each panel marks the ionic liquid band used to normalize IR intensities within the spectral range shown in the figure. (C) also compares transmission (red) and ATR (green) measurements of IR spectra of the same sample of [C₄C₁im][CH₃COO] after the drying process. (D) shows the molar absorption coefficient εₐₘ (black, scale at right), the real part of the refractive index n (green, scale at left), and the imaginary part of the dielectric constant ε″ (red, scale at left) of liquid H₂O as provided by Bertie and Lan.³¹
coordinating anion such as [C4C1im][NTf2]. Otherwise heating is needed to reduce the viscosity and facilitate the drying process for more viscous ionic liquids and more strongly coordinating anions, [C4C1im][CF3SO3] and [C6C1im]-[CH3COO]. It is worth mentioning that increase of temperature implies a certain degree of decomposition as discussed by Gurau et al. for [C4C1im][CH3COO]. Even in a situation where the minor amount of impurity is generated, this heating effect may have a direct consequence in Raman spectroscopy because of eventual increase in fluorescence background. The IR spectra reported by Andanson et al. for [C4C1im][NTf2] and [C6C1im][CF3SO3] and by Thomas et al. and Marekha et al. for [C4C1im][CH3COO] exhibit less intense water bands in comparison with the spectra shown in Figure 5. However, it should be noted that these authors reported IR spectra obtained by ATR while we report transmission IR spectra. In fact, Figure 5C compares transmission and ATR spectra of [C4C1im][CH3COO], the latter exhibiting lower intensity of water bands in comparison with the former, being the spectra normalized by an ionic liquid band. The strong variation of the real part of the refractive index, \( n(\omega) \), within the range of wavenumbers \( \omega \) of an IR absorption (i.e., the so-called anomalous dispersion as illustrated in Figure 5D for liquid water (green line), might imply significant differences between ATR and transmission measurements of IR spectra. The molar absorption coefficient \( E_m \) given by \( E_m = A_{10} / C d \), where \( d \) is the path length, \( C \) is the molar concentration, and \( A_{10} \) is the decadic absorbance following the Beer’s Law, is related to the imaginary part of the refractive index, \( \frac{4\pi n(\omega)}{C} = 2.303 E_m(\omega) \). On the other hand, Stuchebrukhov and Rudoy showed that an ATR spectrum can be considered as the spectrum of the imaginary part of the dielectric constant, \( \varepsilon' \). Since the complex dielectric constant, \( \hat{\varepsilon} = \varepsilon' + i\varepsilon'' \), and refractive index, \( \hat{n} = n + ik \), are related by the fundamental equation \( \hat{n} = \sqrt{\hat{\varepsilon}} \), then \( \varepsilon'(\omega) = n'(\omega) - k^2(\omega) \) and \( \varepsilon''(\omega) = 2n(\omega)k(\omega) \). As a consequence of the anomalous dispersion of \( n(\omega) \) around an IR band, the frequency of the \( \varepsilon''(\omega) \) spectrum is shifted toward the low-frequency side of the band. This is clearly seen in the comparison between ATR and transmission IR spectra of [C4C1im][CF3SO3] shown in Figure 2. Relative intensities of IR bands in ATR and transmission measurements are also affected by the different dependence on the optical constants. This is evident in Figure 5D, which shows \( E_m(\omega) \) and \( \varepsilon''(\omega) \) spectra provided by Bertie and Lan from an investigation of the optical constants of liquid water. It is clear from Figure 5D the difference of intensities in the O–H stretching region for each spectrum. Therefore, the word of caution is that transmission IR spectrum might indicate that an apparent “dry” sample of ionic liquid still contains a significant amount of water, depending on the ionic liquid.

Raman spectra as a function of temperature were obtained in this work for some ionic liquids. We used an OptistatDIN cryostat (Oxford Instruments) filled with liquid nitrogen, thus allowing for the achievement of temperatures as low as 77 K at which ionic liquids are in crystalline or glassy phases. Raman spectra were also obtained for some ionic liquids under pressure within the GPa range by using a diamond anvil cell (DAC). Spectra as a function of pressure at room temperature were obtained with the already mentioned Horiba-Jobin-Yvon T64000 spectrometer having a coupled Olympus BX41 microscope. The Raman spectra were excited with the 647.1 nm laser line focused into the sample by a 20x Leica objective. We used a DAC from Almax EasyLab, model Diacell LeverDAC-Maxi, having a diamond cuvet size of 500 \( \mu \)m. The Boehler microDriller (Almax EasyLab) was used to drill a 250 \( \mu \)m hole in a stainless steel gasket (10 mm diameter, 250 \( \mu \)m thick) preindented to \( \sim 150 \mu \)m. Pressure calibration has been done by the usual method of measuring the shift of the fluorescence line of ruby. Figure 6 illustrates the pressure-dependent fluorescence emission spectra of ruby in the ionic liquid [Pyr14][NTf2]. The inset is a photograph of the DAC chamber containing the ionic liquid sample and ruby spheres used for pressure calibration.

Figure 6. Pressure dependence of the fluorescence emission spectra of ruby in [Pyr14][NTf2]. The inset is a photograph of the gasket hole in between the diamonds of the DAC containing the liquid sample and the ruby spheres used for pressure calibration. In fact, Faria et al. showed that the characteristic [NTf2]– Raman band at 741 cm–1 can be used for pressure calibration. The pressure induced frequency shift of this vibrational mode of [NTf2]– exhibits a linear variation, ca. 4.2 cm–1/GPa, depending on the ionic liquid for pressures up to \( \sim 2.5 \) GPa, so that within this pressure range the ionic liquid can be used as a pressure-transmitting medium and pressure marker.

3. COMPUTATIONAL DETAILS

Polyatomic ions usually involved in forming ionic liquids range from highly symmetric small ions to complex flexible organic ions, so that different theoretical methods have been used for the calculation of vibrational frequencies and normal mode assignment. These include classical normal coordinates analysis relying on an assumed intramolecular force field, ab initio quantum chemistry calculations at different levels of theory for an isolated ion, ion pair or cluster of ions, and molecular dynamics simulation (classical or ab initio) to calculate an appropriate time correlation function and then its Fourier transform to result in the vibrational spectrum. Different methods are chosen not merely on the basis of molecular structure complexity but also on the level of analysis one wishes and approximations allowed for. All of these theoretical methods have been used for assigning vibrational spectra of the most common ions to be discussed in section 4, so that it is 410 useful to provide here a brief account of these methods for future reference along the review.

Classical normal coordinate analysis is based on a ball-and-spring model for the nuclei vibrations with no consideration of electronic degrees of freedom. Taking the [SCN]– anion as
an example, a quadratic force field proposed by Baddiel and Janta\textsuperscript{43} involves internal coordinates for stretching of C–N and C–S bonds, $\Delta_{\text{CN}}$ and $\Delta_{\text{CS}}$, and bending of the SCN angle, $\Delta_{\theta}$,
\begin{equation}
2V = k_{\text{CN}}\Delta_{\text{CN}}^2 + k_{\text{CS}}\Delta_{\text{CS}}^2 + k_{\text{CN,CS}}\Delta_{\text{CN}}\Delta_{\text{CS}} + k_{\phi}\Delta_{\theta}^2.
\end{equation}

(1)

with corresponding force constants $k_{\text{CN}}$, $k_{\text{CS}}$, and $k_{\phi}$ and interaction constant $k_{\text{CN,CS}}$. Force constants are second derivatives of the potential energy function at the equilibrium configuration, and they are optimized in order to reproduce the experimental vibrational frequencies. A normal mode $Q_\alpha$ is a coordinate in which all atoms execute harmonic vibrations with the same frequency leading to a Hamiltonian function, $H = T + V$, where $T$ is the kinetic energy, as a collection of independent oscillators without cross-terms between different coordinates:
\begin{equation}
H = \sum_{\alpha=1}^{3N} \frac{1}{2}(Q_\alpha^2 + \lambda_\alpha Q_\alpha^2).
\end{equation}

(2)

where the eigenvalue $\lambda_\alpha$ of mode $\alpha$ is related to the square of its vibrational frequency, $\nu_\alpha = (2\pi \nu_\alpha)^2$, and the coordinates for convenience are weighted by the square root of atomic masses. The number of nuclei is $N$, and the number of actual vibrational motions, excluding rotational and translational motions of zero frequency, is $3N - 6$ in general or $3N - 5$ for linear molecules.

If this classical Hamiltonian function is used to build the Hamiltonian operator in the quantum chemistry treatment, the set of independent harmonic oscillators implies that the total vibrational energy is the sum of the well-known textbook result for each normal mode, $E_\alpha = \hbar \nu_\alpha$ ($\nu_\alpha = 1/2$, where $\hbar$ is the Planck constant, $\nu_\alpha$ is the vibrational quantum number, $\nu_\alpha = 0, 1, 2 \cdots$, and $\lambda_\alpha$ is the same as the classical vibrational frequency.

Each $Q_\alpha$ is a linear combination of the original coordinates of displacements for all of the atoms of the molecule. The linear combination can be done in terms of the 3N atomic Cartesian coordinates, in terms of internal coordinates of bond-length and angle variations, or in terms of symmetry coordinates, $S_\alpha$. In the so-called method of GF matrices of Wilson, Decius, and Cross,\textsuperscript{41} the symmetry coordinate is a new coordinate system mixing the internal coordinates, so that each $S_\alpha$ belongs to a given symmetry species of the point group of the molecule. The advantage of proposing symmetry coordinates relies on the fact that only $S_\alpha$ of the same symmetry species will mix together in the composition of a given normal mode $Q_\alpha$. Furthermore, defining symmetry coordinates makes easier the resolution of the secular equation for obtaining the eigenvalues because it factors into diagonal blocks for each symmetry species.

In the context of ionic liquids, the classical normal coordinate analysis is more appropriate for simple ions, typically highly symmetric anions. Most of vibrational frequency calculations of ionic liquids referred to in section 4 are based instead on quantum chemistry methods. The electronic structure problem of the molecule is solved within a given approximation for the electronic wave function, and the minimum energy configuration of nuclei is found. For this configuration, one obtains the $3N \times 3N$ Hessian matrix (i.e., the matrix containing second derivatives of potential energy in terms of the nuclei Cartesian coordinates). Diagonalization of the Hessian matrix gives the eigenvalues $\lambda_\alpha$ along the diagonal, and the eigenvector corresponding to each frequency gives the composition of $Q_\alpha$ in terms of atomic displacements.

There are some accounts in the literature of ionic liquids concerning the performance of quantum chemistry methods for calculating different properties (e.g., anion–cation binding energy\textsuperscript{44,45} or gas–ion interactions for studying gas capture by ionic liquids).\textsuperscript{56} On the other hand, there are no benchmark studies for ab initio calculations of vibrational spectra of ionic liquids, although some works provide specific comparisons of vibrational frequencies calculated with different levels of theory.\textsuperscript{47–50} Density functional theory (DFT) is one of the most widely used level of theory for the calculation of vibrational frequencies of ionic liquids since it provides a satisfactory compromise between accuracy and computational time. Overall, the DFT/B3LYP with 6-311++G(d,p) basis set gives good results without being computationally expensive.\textsuperscript{46} Second-order Møller–Plesset perturbation theory (MP2) has been also extensively used in the context of vibrational spectroscopy of ionic liquids. We used these methods to calculate vibrational frequencies for specific purposes of this review.

The ultimate aim of calculating vibrational frequencies is the assignment of vibrational motions to observed frequencies. Most of the works dealing with calculation of vibrational spectra of ionic liquids have interpreted the normal mode composition by direct visualization of atomic displacements on the computer screen. This is a helpful and easy way of assigning the vibrations, although not a quantitative one. Furthermore, it might be misleading because large displacement of hydrogen atoms eventually is only a matter of the small mass of hydrogen but not implying large contribution to the normal mode energy.\textsuperscript{51} Potential energy distribution (PED) in the classical normal coordinate analysis is accomplished by evaluating the percent weight of each symmetry coordinate $S_i$ contributing to the potential energy of the normal mode $Q_\alpha$. The PED can also be written in terms of internal coordinates, an approach which is chemically appealing as one understands the vibrations in terms of changes in bond lengths and angles of valence, out-of-plane, and torsional. Jamróz\textsuperscript{50} made available the computer code VEDA (vibrational energy distribution analysis) which takes the output of the commonly used Gaussian\textsuperscript{51} package of quantum chemistry. The matrices containing atomic displacements and force constants in terms of Cartesian coordinates are available along the calculation of vibrational frequencies with the Gaussian program. The VEDA program then uses the molecular structure, automatically sets internal coordinates, and evaluates how much each one contributes to the energy of a given normal mode. We show in Figure 23 atomic displacements for two normal modes of $[\text{C}_3\text{C}_1\text{C}_1\text{im}]^+$ calculated by the Gaussian program that illustrate the large amplitude of motions of hydrogen atoms, although PED calculated by the VEDA program indicate they contribute little to the normal modes energies.

Harmonic vibrational frequencies are obtained in these ab initio quantum chemistry calculations. No negative eigenvalue (i.e., no imaginary frequency) is obtained as long as the minimum energy molecular structure has been correctly identified. However, theoretical harmonic frequencies are usually higher than experimentally observed, so that scaling factors multiplying the frequencies are needed to bring calculations into agreement with the experiment. Taking 1-alkyl-3-methylimidazolium cations as examples, Talaty et al.\textsuperscript{52} and Heimer et al.\textsuperscript{53} found for $[\text{C}_3\text{C}_1\text{im}]^+\left[\text{PF}_6\right]$ and $[\text{C}_3\text{C}_1\text{im}]^+\left[\text{BF}_4\right]$, $n = 2, 3, \text{ and } 4$, it was necessary to multiply harmonic frequencies calculated by the DFT/B3LYP level of theory by 0.98.
the temperature range are direct probes of the intermolecular dynamics as the positive frequency INM covering the low-frequency not yet for (room temperature) ionic liquids. In atomic molten ZnCl$_2$, in MD simulations of (high temperature) molten salts (e.g. ionic diatomic), carries physical information; for instance, it has been related to thousands of particles is not a minimum energy configuration.

Nevertheless, one still thinks in terms of normal modes because anharmonic effects are taken into account as perturbations on the states and energies of the harmonic model according to perturbation theory of quantum chemistry. The harmonic frequency of a given normal mode continues being related to the force constant as in the harmonic case, but the correction on energy levels mixes $g_{ij}$ and $h_{ij}$ in complicated expressions depending on the order of the expansion of the potential energy function and the order of perturbation theory. Barone et al. made available a code including cubic and quartic anharmonicity constants at second-order perturbation theory (VPT2) to correct harmonic vibrational frequencies calculated by the Gaussian program. Anharmonic frequencies have been indeed calculated by the method of Barone for ionic liquids based on 1-alkyl-3-methylimidazolium cations. The vibrational frequency shift when anharmonicity is included in the calculation of an isolated 1-alkyl-3-methylimidazolium cation might be comparable in magnitude to the effect of considering a cation–anion pair, in particular for those vibrations involving C–H stretching motions. Including anharmonicity not only downshifts vibrational frequencies but also allows for addressing important effects on the experimental spectra (e.g., Fermi resonance). This has been found particularly important in the high-frequency range of vibrational spectra of 1-alkyl-3-methylimidazolium cations because this spectral range is prone to Fermi resonance between overtones or combination bands of ring vibrations with the C–H stretching modes.

The harmonic modeling of expanding the potential energy function to quadratic terms in coordinates has also been proposed for an assembly of molecules forming a liquid. If liquid phase configurations are generated along a computer simulation, either by Monte Carlo (MC) or molecular dynamics (MD), the Hessian matrix can be evaluated for each configuration. Eigenvalues and eigenvectors resulting from the diagonalization of the Hessian matrix give frequencies and composition of normal coordinates for an instantaneous configuration of the liquid, so that these are called instantaneous normal modes (INM). Part of the INM has imaginary frequency because a liquid configuration of thousands of particles is not a minimum energy configuration. Nevertheless, the fraction of imaginary frequency INM also carries physical information; for instance, it has been related to ion-dipole diffusion coefficients. The INM method was applied in MD simulations of (high temperature) molten salts (e.g. ZnCl$_2$, BeCl$_2$, and cryolitic NaF-AlF$_3$ mixtures) but not yet for (room temperature) ionic liquids. In atomic molten salts, the positive frequency INM covering the low-frequency range are direct probes of the intermolecular dynamics as experimentally accessible by far-infrared and low-frequency Raman spectroscopy (see section 5). The INM analysis of molten ZnCl$_2$ was useful to disentangle collective soundlike modes and localized vibrational modes of a molecular-like structure of ZnCl$_2$ tetrahedral. In the case of BeCl$_2$ and NaF-AlF$_3$, mixtures, INM of frequencies up to $\sim$1000 cm$^{-1}$ are obtained because of relatively stable [BeCl$_2$_n]$_n$ oligomers and AlF$_n$ polyhedrals.

Dynamical effects are not included in a quantum chemistry calculation of vibrational spectrum once it is carried out in a minimum energy configuration of an isolated ion, an ionic pair, or a cluster of ions. In contrast, the theoretical framework of time correlation function is appropriated for calculating vibrational spectra by MD simulations of liquids. A time correlation function measures how a system property at a given time, $A(t)$, correlates with another property at a previous time, $B(0)$. In an autocorrelation function, $C_n(t) = \langle A(t) \cdot A(0) \rangle$, where $\langle \cdots \rangle$ indicates an average according to statistical mechanics, $C_n(t)$ starts from $\langle |A(1)|^2 \rangle$ at time zero and reaches the long time value $\langle |A| \rangle^2$. Figure 7 illustrates the behavior of a time correlation function for the atomic velocities, $C_n(t) = \langle \psi_0(t) \cdot |\psi(t)\rangle$, calculated by MD simulation of [C$_6$C$_2$im][NTf$_2$]. The intra- and intermolecular potential function we used in this simulation is the CL&P model proposed by Lopes and Padua.

![Figure 7](image-url)

Figure 7. Upper panel: power spectra, $P(\omega)$, calculated according to eq 3 by classical MD simulation of [C$_6$C$_2$im][NTf$_2$] at 400 K and density 1.05 g cm$^{-3}$. The MD simulation considered 500 ion pairs and the CL&P force field. The total $P(\omega)$ (black line) has been split into contributions of atoms belonging to anions (red line) and cations (green line). Intensity was normalized by the most intense band of each $P(\omega)$. The inset highlights the low-frequency range of the total $P(\omega)$. Bottom panel: the normalized time correlation functions of velocity, $C_n(t)$, obtained from the Fourier transform of the corresponding power spectrum. The inset shows the total $C_n(t)$ in a wider time range.
for MD simulations of ionic liquids.\textsuperscript{75} Figure 7 shows $C_\ell(t)$, including all of the atoms $\ell$, and also $C_\ell(t)$ calculated separately for atoms belonging to either cations or anions. The $C_\ell(t)$ is shown normalized by its initial value, decaying to the average value of velocity which is zero. Figure 7 also shows the so-called power spectrum, $P(\omega)$ (i.e., the density of vibrational states). Given any time-dependent property $A(t)$, its power spectrum $P_A(\omega)$ can be obtained as the Fourier transform of the corresponding time correlation function, $C_A(t) = \langle A(0) \cdot A(t) \rangle$. An alternative method to calculate $P_A(\omega)$ more efficiently follows from the spectral density of $A(t)$:\textsuperscript{74,76–78}

$$P_A(\omega) = | \int_{-\infty}^{\infty} A(t) e^{-i\omega t} dt |^2$$ \hfill (3) 

Then, the $C_A(t)$ can be obtained by Fourier transforming the $P_A(\omega)$. The $C_A(t)$ shown in the inset of the bottom panel of Figure 7 exhibits an overall damped oscillatory decay within the picosecond time range, arising from rattling dynamics of ions within a temporary cage made of neighboring ions. This intermolecular dynamics is manifested in the $P(\omega)$ within the frequency range below ca. 100 cm$^{-1}$ (see inset in the top panel of Figure 7), which is the range accessible by far-IR and low-frequency Raman spectroscopy. The CL&P model considers flexible ions, so that the very fast oscillations in $C_A(t)$ (main figure at the bottom panel of Figure 7) arise from the intramolecular vibrations. Accordingly, $P(\omega)$ shows high-frequency peaks assigned to cation and anion intramolecular vibrations.

Vibrational frequencies in $P(\omega)$ manifest condensed phase and anharmonicity effects, as long as an anharmonic intramolecular potential function is included in the model. It is worth noting, however, that the CL&P model\textsuperscript{75} considers harmonic terms for stretching and bending motions. On the other hand, it is well-known that proper coupling between intra- and intermolecular degrees of freedom, and the consequence vibrational frequency shift and vibrational relaxation in the liquid with respect to the gas phase, is heavily dependent on anharmonic terms in the intramolecular potential.\textsuperscript{79–81} Calculations of $P(\omega)$ have been done by ab initio MD simulations,\textsuperscript{32,78} which do not rely on an empirical parametrized force field, instead the electronic structure is solved along the simulation run giving the forces that move the nuclei to the new configuration. Therefore, anharmonicity of vibrations is taken into account when $P(\omega)$ of ionic liquids are calculated by ab initio MD simulations.

The power spectrum shown in Figure 7 is not a theoretical IR or Raman spectrum.\textsuperscript{78} $P(\omega)$ exhibits all of vibrations included in the model, and it has to be weighted by how much the intra- and intermolecular dynamics fluctuate the electric dipole moment or the polarizability in order to represent the IR or the Raman spectrum, respectively. In other words, IR and Raman activities are determined by the coupling between mechanical vibrations and electronic molecular properties. It is a formal result of nonequilibrium statistical mechanics that the IR spectrum, $I_{IR}(\omega)$, is proportional to the Fourier transform of the time correlation function of fluctuations of the electric dipole moment of the whole system:

$$I_{IR}(\omega) \propto \int_{-\infty}^{\infty} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle e^{i\omega t} dt$$ \hfill (4) 

$\mathbf{M}(t)$ may be approximated at first order as the sum of individual molecular dipole moments, although induced interaction effects imply that $\mathbf{M}(t)$ is a collective property.\textsuperscript{82}

An expression analogous to eq 4 follows for the Raman spectrum as the Fourier transform of the time correlation function of polarizability fluctuation. The alternative method of eq 3 also applies to the calculation of IR or Raman spectrum from the time-dependence of dipole moment or polarizability. Vibrational spectra result from time correlation functions of dipole moment or polarizability fluctuations calculated by ab initio MD simulations resulting in reasonable agreement to experimental spectra of ionic liquids.\textsuperscript{33} This approach for calculating vibrational spectra of liquids has been implemented in the TRAVIS (Trajectory Analyzer and VISualizer) package,\textsuperscript{83} which includes several routines for analyzing trajectories generated by computer simulations.

The time correlation function approach for vibrational spectroscopy allows for a direct comparison between simulation and experiment in terms of peak positions, band shapes, and relative intensities, but the ultimate goal of the normal mode assignment is not yet reached. One possibility is to take a few liquid configurations generated by the MD simulation for energy minimization using, for instance, the conjugate gradient method.\textsuperscript{84,85} In contrast to the INM analysis discussed above, this approach calculates the Hessian matrix and performs the normal-mode analysis for those quenched configurations. In the time correlation function approach, however, the actual nature of the molecular vibration responsible for a given band should be retrieved from the spectrum obtained from the Fourier transform. A generalized normal coordinates approach\textsuperscript{86,87} has been applied for an anharmonic Hamiltonian as it is the case in ionic liquids forming organic cations. The approach is based on a generalization of $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$, which is a single particle time correlation function as it involves the property of a given particle $i$. The generalization accounts for calculating the collective counterpart of mass-weighted velocities, $\langle \mathbf{m}_i \mathbf{v}(0) \cdot \mathbf{m}_i \mathbf{v}(t) \rangle$, whose Fourier transform gives a power spectrum $P_{\mathbf{v}}(\omega)$, including cross-correlations between different particles.\textsuperscript{68} The matrix relating Cartesian to the generalized normal coordinates is obtained according to a recipe which minimizes off-diagonal terms of $P_{\mathbf{v}}(\omega)$ for all of the frequencies. The procedure brings the collective power spectrum as close as possible to a diagonal form leading to a representation of vibrations in terms of normal modes. This approach for calculating normal modes from computer simulation includes anharmonicity and condensed phase effects, and it has been applied to assign vibrational spectra of $[C_2H_5][CH_3COO]$ and its mixture with CO$_2$ and water.\textsuperscript{33}

4. VIBRATIONAL SPECTROSCOPY OF PURE IONIC LIQUIDS IN THE MID-FREQUENCY RANGE

4.1. Vibrational Frequencies of Anions

4.1.1. Small Symmetric Anions. Vibrational spectroscopy is of long usage for studying (high temperature) molten salts of polyatomic inorganic anions, some of which are common in ionic liquids. Reliable assignment of vibrational frequencies is needed in order to use IR and Raman spectroscopies as useful tools for unravelling molecular conformations, intermolecular interactions, hydrogen bonds, etc. The highly symmetric structures of inorganic anions allow for more straightforward assignment of vibrational frequencies in comparison with the ionic liquids forming organic cations.
The very fact that anion vibrational frequencies increase with comparison with the vibrational frequency of the free species. 

There is accumulated knowledge on how vibrational frequencies of anions depend on cation charge and size, solid–liquid phase transition, temperature, and dilution in solvents of different dielectric constants. Vibrational frequency of stretching motion of simple anion decreases when the cation is replaced by another with lower polarizing power (i.e., the ratio between charge and ionic radius of the cation). In terms of mechanical models of balls and springs, vibrational frequency shift in the condensed phase is a subtle balance between attractive and repulsive intermolecular forces contributing, respectively, to negative and positive shift in comparison with the vibrational frequency of the free species. The very fact that anion vibrational frequencies increase with strength of interaction with the cation points out the role played by short-range repulsive forces on the probe oscillator. As ionic liquids are usually made of bulky organic cations, the anion stretching mode is expected at lower frequency than molten salts based on alkali cations. For instance, the vibrational frequency of the totally symmetric stretching mode of the nitrate anion, $\nu_\text{as}(\text{NO}_3^-)$, in molten alkaline nitrates (at $T \sim 400$ °C) exhibits a significant downward shift from 1067 to 1043 cm$^{-1}$ when the counterion is changed along the sequence of Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$. Accordingly, $\nu_\text{as}(\text{NO}_3^-)$ is observed at 1041 cm$^{-1}$ in molten [C$_4$C$_1$im][NO$_3^-$] at 313 K. 

Analogous effect of cation polarizing power is found in the CN stretching mode of [$\text{SCN}^-$]. In molten LiSCN, NaSCN, and KSCN, $\nu(\text{CN})$ follows the trend 2083, 2074, and 2068 cm$^{-1}$. Arguing beyond mechanical springs–and–balls models, Chabanel et al. claimed that strongly polarizing cations stabilize the anion $^\sigma$ orbitals. This effect of strengthening the CN bond is partially counterbalanced by the effect of resonance structures, $^\delta$S–C≡N $\leftrightarrow$ $^\delta$S=C=N, that softens the CN bond and becomes predominant as larger is the cation. Accordingly, the $\nu(\text{CN})$ mode is observed at 2054 cm$^{-1}$ in

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### Table 1. Fundamental Frequencies of Some Highly Symmetric Anions Commonly Used in Ionic Liquids$^a$

<table>
<thead>
<tr>
<th>Anion</th>
<th>IR</th>
<th>Raman</th>
<th>$D_{\alpha}$</th>
<th>IR</th>
<th>Raman</th>
<th>$T_d$</th>
<th>IR</th>
<th>Raman</th>
<th>$O_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO$_3^-$]</td>
<td>1346 vs</td>
<td>$\nu_\text{as}(E')$</td>
<td>1062 vs</td>
<td>$\nu_\text{as}(F_2)$</td>
<td>843 vs</td>
<td>$\nu_\text{as}(F_{1u})$</td>
<td>741 m$^b$</td>
<td>$\nu_\text{as}(F_{1u})$</td>
<td>565 w$^b$</td>
</tr>
<tr>
<td></td>
<td>1041 w$^b$</td>
<td>$\nu_\text{as}(A_1')$</td>
<td>764 m$^b$</td>
<td>$\nu_\text{as}(A_1')$</td>
<td>740 vs</td>
<td>$\nu_\text{as}(F_{1u})$</td>
<td>568 m</td>
<td>$\nu_\text{as}(F_{1u})$</td>
<td>560 w$^b$</td>
</tr>
<tr>
<td>[BF$_4^-$]</td>
<td>830 m</td>
<td>$\gamma(A_1')$</td>
<td>522 m</td>
<td>$\delta(F_2)$</td>
<td>558 s</td>
<td>$\delta(F_{2u})$</td>
<td>470 w$^b$</td>
<td>$\delta(F_{2u})$</td>
<td>471 m</td>
</tr>
<tr>
<td>[PF$_6^-$]</td>
<td>708 w</td>
<td>521 w</td>
<td>352 w</td>
<td>$\delta(E')$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Values (cm$^{-1}$) correspond to frequencies observed in IR and Raman spectra at room temperature for ionic liquids with the [C$_4$C$_1$im]$^+$ cation for anions and the [C$_2$C$_1$im]$^+$ cation for the cyanate anions. $\nu$, stretch; $\delta$, bend; $\gamma$, out-of-plane; s, symmetric; as, antisymmetric; w, weak; m, medium; s, strong; v, very. Inactive according to the symmetry of isolated species.

Figure 8. IR (red, transmittance scale at right) and Raman (black) spectra of [C$_4$C$_1$im][BF$_4^-$] (left panel) and [C$_4$C$_1$im][PF$_6^-$] (right panel) at room temperature in the range of the totally symmetric stretching mode of the anion.
The anion vibrational properties are an issue in vibrational spectroscopy of ionic liquids. The band range of a Raman band exhibits exponential shape. A particular effect is an exponential long tail, $e^{-\omega/\Delta}$, where $\Delta$ is a parameter, in a Raman band corresponding to a normal mode which is allowed by symmetry of the isolated molecule. Depolarized Raman spectra have been interpreted by assuming there is time separation between fast rattling dynamics of molecules within the cage of neighbors, resulting in interaction-induced effect as intermolecular distances are changed, and slow reorientational dynamics of the molecule as a whole. The short-time rattling dynamics contributes to the high-frequency tail of the band, whereas the relatively slow reorientational dynamics contributes to the center of the band. Unfortunately, there are overlaps of bands in vibrational spectra of ionic liquids, being difficult to address whether the high-frequency range of a Raman band exhibits exponential shape. A particular band that could be considered in this respect is the stretching mode $\nu(CN)$ of $[SCN^-]$ because it appears in a spectral range free of overlaps. Figure 9 shows the depolarized $\nu(CN)$ Raman band of $[C_4C_1im][SCN]$ at room temperature. The $\nu(CN)$ Raman band indeed exhibits a long tail which extends far from the band-center. The inset of Figure 9 makes clear that the tail exhibits the exponential shape, strongly suggesting that interaction-induced mechanisms should not be ruled out. It would be interesting for future work attempts to disentangle symmetry reduction and interaction-induced effects in vibrational spectroscopy of ionic liquids.

Classical intramolecular force fields for computing vibrational frequencies are available for some ionic liquid forming anions (e.g., $[NO_3^-]$, $[SCN^-]$, and $[C(CN)_3]^-$). On the other hand, the complex molecular structures of the ions typically involved in ionic liquids prompt for quantum chemistry as the more appropriate approach to calculate vibrational frequencies. Hipps and Aplin accounted for the vibrations of $[C(CN)_3]^-$.
in the potassium salt with a quadratic force field with force
constants for internal coordinates of bond displacements and 
angles based on ab initio calculation. The carbon–carbon
distance and force constant obtained for [C(CN)3]− are similar
to values for benzene, indicating significant resonance
stabilization in [C(CN)3]−. We have found bands at 1231
and 1230 cm−1 in IR and Raman spectra, respectively, of
[C2C1im][C(CN)3]. In accordance with the assignment
suggested by Hipps and Aplin for simpler [C(CN)3]−
salts,105 this is a combination band intensified by Fermi
resonance with the fundamental E′ mode observed at 1257
9999 cm−1 in IR and Raman spectra of [C2C1im][C(CN)3]. The
occurrence of this Fermi resonance was indeed confirmed by
anharmonic ab initio calculations of an isolated [C(CN)3]−
anion performed in this work (MP2/VPT2 level of theory, aug-
cc-pVDZ basis set). The calculation showed that the 1230 cm−1
band is the combination of A′ + δ(CCN) and E′ ν(C–C–N)
99999 modes calculated at 606 and 641 cm−1, respectively.

The vibrational frequency of the totally symmetric CN
stretching mode decreases along the sequence [B(CN)4]−,
9999 [C(CN)3]−, and [N(CN)2]− as the electronic de-localization
increases by 2223, 2209, and 2192 cm−1, respectively, in ionic
999999 liquids with the same [C2C1im]− cation (see Figure 10).100 In
an IR spectroscopy study of solid [NH4][N(CN)2], Sprague et
al.107 assigned the nontotally symmetric mode νas(C≡N) at
99999999 higher frequency than the totally symmetric mode νs(C≡N). It
99999999 is a rule of thumb in vibrational spectroscopy assigning the
99999999 nontotally symmetric stretching at higher frequency than the
totally symmetric stretching of a given moiety. However, the
opposite is true for [N(CN)2]− and [C(CN)3]−. The IR,
99999999 polarized, and depolarized Raman spectra shown in Figure 10
99999999 for [C2C1im][N(CN)2] and [C2C1im][C(CN)3] in the spectral
range covering νas(C≡N) and νs(C≡N) modes support the
assignment. Crystallographic analysis108 of Li[N(CN)2] showed
that the N–C bond length (131 pm) is in between
typical values for single and double bonds, whereas the C≡N
999999 bond length (116 pm) is in between double and triple bonds.
999999 Therefore, Reckeweg et al.109 concluded that the electronic
structure is better represented as the resonance hybrid "N=N
999999 C≡N=C≡N ↔ N=C≡N≡C≡N," rather than "N=C
999999 N≡C=C≡N." On the basis of this resonance, it is reasonable that
999999 a vibration will be of lower energy when the two CN moieties
999999 oscillate antisymmetrically. The IR spectrum of [C2C1im][N−
999999 (CN)3] exhibits another band at 2227 cm−1 (just out of
the spectral window shown in Figure 10), which has been
assigned109 to a combination band of νs(N=C) and νas(N=C)
c modes whose frequency is shifted and intensity is enhanced
999999 because of the Fermi resonance with the fundamental of the
νas(CN) mode. In the case of [B(CN)4]−, the Raman active
999999 ν(CN) and the IR active νas(CN) are observed at the same
frequency.110

4.1.2. More Complex Fluorinated Anions. The bis-
(trifluoromethanesulfonyl)imide, [NTf2]−, is one of the most
999999 popular anions, resulting in low melting point salts when
999999 combined with the majority of common organic cations.19
999999 Assignment of vibrational frequencies of [NTf2]− has been an
999999 issue in the literature because the lithium salt of [NTf2]− is
999999 commonly used in polymer electrolytes. Rey et al.111 provided a
detailed analysis of the [NTf2]− normal modes on the basis of
999999 quantum chemistry calculations for its C2 conformer. In a 999999
999999 subsequent IR and Raman spectroscopic study, Herstedt et
99999999 al.112 were able to distinguish bands characteristic of C2 and C9
99999999 conformers of [NTf2]−, commonly called transoid and cisoid,
respectively, in solutions of Li[NTf2] in ethers CH3O–
99999999 (CH2CH2O)nCH3, where n = 1, 2, 3, and 4. A complete
99999999 table of experimental versus calculated vibrational frequencies,
99999999 internal force constants, and potential energy distribution of
99999999 [NTf2]− normal modes can be found in these papers.111,112
99999999
99999999 Some of the bands assigned to [NTf2]− vibrations actually
99999999 observed in IR and Raman spectra of a typical ionic liquid,
99999999 [C2C1im][NTf2], are marked in Figure 11. Tables containing
99999999 the [NTf2]− vibrational frequencies are available in many
99999999 papers,111,112-123 but values strongly depend on the counterion,
physical state, and solvent. Thus, Table 2 lists the actual values
99999999 observed in [C2C1im][NTf2] at room temperature. The
99999999 eigenvectors of [NTf2]− normal modes exhibit a complex
99999999 pattern involving displacements of many atoms, so that the
assignment in Table 2 is only a simplification of the potential

Figure 10. IR (red, transmittance scale at right) and Raman spectra (black; full line, polarized; dashed line, depolarized) of ionic liquids
[C2C1im][N(CN)2] (left), [C2C1im][C(CN)3] (middle), and [C2C1im][B(CN)4] (right) at room temperature.
Raman spectroscopy unveiling the coexistence of transoid and cisoid \([\text{NTf}_2^-]\) conformers in the normal liquid phase of ionic liquids. Ionic liquids in which \([\text{NTf}_2^-]\) conformers have been found by vibrational spectroscopy include systems based on derivatives of imidazolium, \(^{119,124,125}\) pyrrolidinium, \(^{116,118}\) piperidinium, \(^{120}\) and ammonium. \(^{122,123,128}\) Quantum chemistry calculations indicate that the spectral ranges 260–370 cm\(^{-1}\) and 620–660 cm\(^{-1}\) are well-suited for finding bands that characterize the transoid or the cisoid conformation. These spectral ranges of the Raman spectrum of \([\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]\) are highlighted in Figure 12. The antisymmetric SO\(_2\) out-of-plane bending at 623 cm\(^{-1}\) characterizes the transoid conformer, whereas the S–N–S bending at 650 cm\(^{-1}\) characterizes the cisoid conformer. These are very weak Raman bands so that the 260–370 cm\(^{-1}\) range is more appropriated for identifying the \([\text{NTf}_2^-]\) conformation. In particular, the SO\(_2\) rocking at 326 cm\(^{-1}\) is characteristic of the cisoid conformer. The quantum chemistry assignments marked in Figure 12 are supported by 1002 remarkable spectral changes eventually observed in crystalline phases as bands belonging to a given conformer might be absent. Following phase transitions of ionic liquids by vibrational spectroscopy will be discussed in section 6. The most intense Raman band at 741 cm\(^{-1}\), corresponding to a normal mode in which the \([\text{NTf}_2^-]\) anion breathes as a whole, 1008 exhibits an asymmetric band shape that has been also assigned to transoid and cisoid conformers, giving two components with a small difference of \(\sim 3\) cm\(^{-1}\).\(^{116}\) On the other hand, it will be 1011

Table 2. Vibrational Frequencies of Some Fluorinated Anions Commonly Used in Ionic Liquids

<table>
<thead>
<tr>
<th>Anion</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{NTf}_2^-])</td>
<td>120</td>
<td>(\nu(CF_3))</td>
</tr>
<tr>
<td>([\text{N(SO}_2\text{F})_2^-])</td>
<td>291</td>
<td>(\nu(SO_2))</td>
</tr>
<tr>
<td>([\text{CF}_3\text{SO}_3^-])</td>
<td>297</td>
<td>(\rho(CF_3))</td>
</tr>
</tbody>
</table>

Values (cm\(^{-1}\)) correspond to frequencies observed in IR and Raman spectra at room temperature for ionic liquids with the \([\text{C}_2\text{C}_1\text{im}]+\) cation for \([\text{NTf}_2^-]\) and \([\text{N(SO}_2\text{F})_2^-]\) anions and the \([\text{C}_2\text{C}_1\text{im}]+\) cation for \([\text{CF}_3\text{SO}_3^-]\): \(\nu\), stretch; \(\delta\), bend; \(\delta_{\text{sc}}\), scissoring; \(\omega\), twisting; \(\rho\), rocking; \(\tau\), torsion; \(s\), symmetric; \(a\), antisymmetric; \(ip\), in plane; and \(op\), out-of-plane.
discussed that the 741 cm$^{-1}$ band is very sensitive to coordination of [NTf$_2]$$^-$ to small cations of high polarizing power (see section 7).

The closely related bis(fluorosulfonyl)imide anion, [N-(SO$_2$F)$_2$]$^-$, also exhibits equilibrium between C$_1$ and C$_2$ conformers in ionic liquids. Fujii et al. discussed the signature of conformational equilibrium of [N(SO$_2$F)$_2$]$^-$ in vibrational spectra of ionic liquids containing the cations 1-ethyl-3-methylimidazolium and N-methyl-N-propyl-pyrroli-

dium. Figure 13 shows vibrational spectra of [C$_2$C$_1$im][N(SO$_2$F)$_2$] with the anion bands indicated by arrows. Assignment of [N(SO$_2$F)$_2$]$^-$ normal modes has not been provided in refs. and the work of Matsumoto et al. concerning polymorphism in crystals of Na$, K^+$, and Cs$^+$. On the basis of quantum chemistry calculations at the DFT/B3LYP level of theory, Fujii et al. proposed that Raman bands of [N(SO$_2$F)$_2$]$^-$ in the range of 250–400 cm$^{-1}$ are asymmetric because of the presence of both the [N(SO$_2$F)$_2$]$^-$ conformers. The bands seen in Figure 14 at 291, 326, and 359 cm$^{-1}$ in the Raman spectrum of [C$_2$C$_1$im][N(SO$_2$F)$_2$] correspond to SO$_2$F out-of-plane bending for cisoid conformer.

Figure 12. Raman spectrum of [C$_2$C$_1$im][NTf$_2$] in the spectral ranges covering the bands characteristics of [NTf$_2$]$^-$ in transoid (marked #) and cisoid (marked *) conformations. Optimized structures of transoid and cisoid conformers of [NTf$_2$]$^-$ are shown.

Figure 13. IR (red, transmittance scale at right) and Raman spectra (black) of [C$_2$C$_1$im][N(SO$_2$F)$_2$] at room temperature. Some bands assigned to [N(SO$_2$F)$_2$]$^-$ normal modes are indicated by arrows.

Figure 14. Raman spectrum of [C$_2$C$_1$im][N(SO$_2$F)$_2$] at room temperature. Vibrational frequencies and relative intensities of Raman bands calculated by the DFT/B3LYP level of theory are indicated for [N(SO$_2$F)$_2$]$^-$ at C$_1$ (cisoid, blue lines) and C$_2$ (transoid, red lines) conformation. Optimized structures of transoid and cisoid conformers of [N(SO$_2$F)$_2$]$^-$ are shown.
or SO$_2$F twisting for transoid conformer, SO$_2$ rocking for cisoid conformer or SO$_2$F out-of-plane bending for transoid conformer, and SO$_2$F in-plane bending for cisoid conformer or SO$_2$F out-of-plane bending for transoid conformer, respectively.\textsuperscript{131} The calculated frequencies for each [N(SO$_2$F)$_2$]$^-$ conformer are relatively close, so that the more strong experimental evidence in favor of conformational equilibrium in the ionic liquid is the temperature dependence of the spectral pattern.\textsuperscript{129,130,132} The relative intensities of components belonging to transoid conformer decrease with increasing temperature providing support to the calculations that transoid is the lower energy conformer between them.\textsuperscript{129,130}

Giffin et al.\textsuperscript{133} prepared pyrrolidinium ionic liquids with an anion whose molecular structure lies in between [NT$_6^-$] and [N(SO$_2$F)$_2$]$^-$, namely, (fluorosulfonyl) trifluoromethanesulfonfyl)imidide, [N(SO$_2$F) (CF$_3$SO$_2$)$_2$]$^-$. The most intense Raman band of [N(SO$_2$F) (CF$_3$SO$_2$)$_2$]$^-$, at 730 cm$^{-1}$ is the counterpart of the characteristic band due to the expansion and contraction modes of [NT$_6^-$]. Giffin et al.\textsuperscript{133} emphasized that this band of [N(SO$_2$F) (CF$_3$SO$_2$)$_2$]$^-$ is broader than analogous band of [NT$_6^-$] proper to distribution of three rotamers of [N(SO$_2$F) (CF$_3$SO$_2$)$_2$]$^-$. The authors of ref 133 provided a table of experimental versus calculated vibrational frequencies and normal mode assignment for different conformers of [N(SO$_2$F) (CF$_3$SO$_2$)$_2$]$^-$, but overlap of bands in the spectral range 280–400 cm$^{-1}$ implies that distinguishing the presence of [N(SO$_2$F) (CF$_3$SO$_2$)$_2$]$^-$ conformers by Raman spectroscopy is a more challenging task than [NT$_6^-$] conformers.

The trifluoromethanesulfonfyl (triflate) anion, [CF$_3$SO$_3$]$^-$, was the subject of many vibrational spectroscopy studies because it has been extensively used in polymer electrolytes.\textsuperscript{134–137} One recurrent issue in these works is to unveil, from frequency shift and band split, ionic pairing between different anions or [CF$_3$SO$_3$]$^-$ and alkali metal cations. Here again vibrational frequencies of some normal modes are very dependent on the polarizing power of the cation. For instance, frequencies of some normal modes are very sensitive to the potential energy distribution of the anion whose molecular structure lies in between [NT$_6^-$] and [N(SO$_2$F)$_2$]$^-$ as found in aqueous solution of Na[C$_2$SO$_4$].\textsuperscript{149} In ref148, the authors of ref 133 discussed in an IR and Raman study by Mao and Damodoran\textsuperscript{146} the vibrations of tris(pentafluoroethyl)-trifluorophosphate, [FAP]$^-$, in the ionic liquid [C$_2$C$_1$im][FAP] have been discussed in an IR and Raman study by Mao and Damodoran\textsuperscript{146} and in an IR study by Voroshylova et al.\textsuperscript{147} These two works provide a full list of observed frequencies of [C$_2$C$_1$im][FAP] and assignments based on the potential energy distribution of normal modes calculated for the ionic pair at the DFT/B3LYP level of theory. Concerning those bands belonging to [FAP]$^-$ normal modes, there are some disagreement on assignments proposed in these works. For example, the intense IR band at 1209 cm$^{-1}$ was assigned to $\nu$(C) by Mao and Damodoran,\textsuperscript{146} but to $\nu$(CF) by Voroshylova et al.\textsuperscript{147} Two isomers of [FAP]$^-$ are possible, meridional and facial, each one with several conformers. The calculations of Voroshylova et al.\textsuperscript{147} indicated IR bands at ~800 and ~700 cm$^{-1}$ as characteristic features of meridional and facial isomers, respectively, and mixture of anion conformers in [C$_2$C$_1$im][FAP].

4.1.3. AlkylSulfates and Hydrogen Sulfate. Few works have discussed vibrational spectra of pure ionic liquids containing alkylsulfate anions, [R–O–SO$_3$]$^-$, in spite of the relevance of this class of anion forming ionic liquids. IR and Raman spectra of 1-ethyl-3-methylimidazolium ethylsulfate [C$_2$C$_1$im][C$_2$SO$_4$],\textsuperscript{126} [C$_2$C$_1$im][C$_6$SO$_4$], have been first discussed by Kiefer et al.\textsuperscript{115} and in a subsequent paper by Dhumal et al.\textsuperscript{148} The IR frequencies listed in these two works agree with each other; however, there is systematic mismatching between them for the Raman frequencies of [C$_2$C$_1$im][C$_6$SO$_4$].\textsuperscript{149} In light of disagreement of reported frequencies for [C$_6$SO$_4$]$^-$,\textsuperscript{115} Figure 16 shows IR and Raman spectra obtained in this work for [C$_2$C$_1$im][C$_6$SO$_4$] at room temperature. Raman frequencies of [C$_2$C$_1$im][C$_6$SO$_4$] we obtained agree with values given in ref 148.\textsuperscript{139} Dhumal et al.\textsuperscript{148} calculated vibrational frequencies at the DFT/B3LYP level of theory for isolated ions and the ionic pair.
Assignment of vibrational frequencies on the basis of comparison between calculated and experimental data is particularly difficult for this system because strong anion–cation interaction imply significant frequency shifts. For instance, the most intense and sharp Raman band at ~1060 cm\(^{-1}\), which is assigned to S–O symmetric stretching of \([\text{C}_2\text{SO}_4]\) in ref 149, is assigned to C–O stretching in ref 148. In this work, we calculated vibrational frequencies of an ionic pair made of \([\text{C}_2\text{SO}_4]^-\) and tetramethylammonium cation at the DFT/B3LYP level of theory with a basis set 6-311+ +G(d,p). Our results are inline with the assignment of Dhumal et al.,150 that is, the Raman bands observed at 1061.5 and 959 cm\(^{-1}\) at 1010 cm\(^{-1}\) have also been found, whose intensity increases as temperature decreases, and assigned to \([\text{HSO}_4]\)^− engaged in chains of hydrogen-bonded anions.156 Signature of anion–cation hydrogen bonding has been found in vibrational spectra of alkali bisulfate crystals.157–156 It had been proposed decades ago that simple \([\text{HSO}_4]\)^− molten salts are very viscous because structures of hydrogen-bonded anions existing in the crystalline phase remain in the liquid phase just above the melting temperature. Therefore, it was proposed that the very high viscosity of \([\text{HSO}_4]\)^− ionic liquids in comparison with alkylsulfates for a given 1-alkyl-3-methylimidazolium cation is due to anion–anion, rather than anion–cation, hydrogen bonding.

4.1.4. Carboxilates. Vibrational spectroscopic studies of carboxylate-based ionic liquids are heavily linked to applications in gas absorption to be discussed in section 7. Here we focus on vibrational frequencies of acetate in pure ionic liquids based on 1-alkyl-3-methylimidazolium cations. IR and Raman spectra of \([\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{COO}]\) and \([\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{COO}]\) have been discussed by Thomas et al.133 and Cabaço et al.,162 respectively. Raman frequencies of \([\text{CH}_3\text{COO}]^-\) reported in these works are listed in Table 3 showing some inconsistencies between them. Ito and Bernstein163 discussed IR and Raman spectra of aqueous solutions of formate, oxalate, and acetate; the vibrational frequencies of the latter are given in Table 3 for comparison purposes. Assignment of \(\nu_1(\text{COO})\) and \(\nu_2(\text{COO})\) modes in ionic liquids \([\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{COO}]\) is cumbersome because of overlaps with bands of imidazolium ring modes in the same spectral range. A large number of works address vibrational spectra of acetate in alkali salts and metal

### Table 3. Fundamental Frequencies (cm\(^{-1}\)) and Assignments Reported in the Literature for Raman Spectra of the Acetate Anion in Ionic Liquids. Raman Frequencies of Na[CH\(_3\)COO] Aqueous Solution are Given for Comparison Purposes

<table>
<thead>
<tr>
<th>Thomas et al.(^{33}) ([\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{COO}])</th>
<th>Cabaço et al.(^{162}) ([\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{COO}])</th>
<th>Ito and Bernstein(^{163}) Na[CH(<em>3)COO] (</em>{\text{(aq)}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>635</td>
<td>(\delta(\text{OCO})+\nu_1(\text{CC}))</td>
<td>454</td>
</tr>
<tr>
<td>899</td>
<td>(\delta(\text{OCO})+\nu_1(\text{CC}))</td>
<td>637</td>
</tr>
<tr>
<td>1334</td>
<td>(\nu_1(\text{COO}))</td>
<td>902</td>
</tr>
<tr>
<td>1567</td>
<td>(\nu_2(\text{COO}))</td>
<td>1326</td>
</tr>
<tr>
<td>1382</td>
<td>(\nu(\text{COO}))</td>
<td>1382</td>
</tr>
<tr>
<td>1582</td>
<td>(\nu_2(\text{COO}))</td>
<td>2917</td>
</tr>
<tr>
<td>2917</td>
<td>(\nu_1(\text{CH}_3))</td>
<td>2936</td>
</tr>
</tbody>
</table>

*For comparison purposes, corresponding Raman frequencies of Na[CH\(_3\)COO] aqueous solution are given with their assignment and symmetry. \(\nu\), stretch; \(\delta\), bend; \(\rho\), rocking; \(s\), symmetric; \(as\), antisymmetric; \(ip\), in plane.*
However, direct comparison with the frequencies observed in ionic liquids is not straightforward since [CH₃COO]⁻ frequencies are very sensitive to coordination. Furthermore, theoretical calculations for [C₄C₁im][CH₃COO] in the gas phase might lead to proton transfer and formation of the N-heterocyclic carbene. This is regarded as an important step along the process of CO₂ absorption, but the theoretical tool employed by Thomas et al.³³ was ab initio molecular dynamics simulation of 36 pairs of [C₄C₁im][CH₃COO] ions, whereas Cabaço et al.¹⁶² performed DFT/B3LYP calculations of a cluster made of two pairs of [C₄C₁im][CH₃COO]⁻[CH₃COO]⁻ ions. In order to identify the CH₃COO⁻ bands, it is useful to compare vibrational spectra of acetate-based and other ionic liquids with the same cation. Cabaço et al.¹³ compared IR and Raman spectra of [C₄C₁im][CH₃COO], [C₄C₁im][BF₄]²⁻, and [C₄C₁im][PF₆]²⁻.

In Figure 17, we provide a comparison of IR and Raman spectra of [C₄C₁im]⁻[CH₃COO] at room temperature. For comparison purposes, IR (red) and Raman (black) spectra of [C₄C₁im][BF₄]²⁻ and [C₄C₁im][PF₆]²⁻ are shown. Arrows indicate bands assigned to [CH₃COO]⁻ normal modes.

Three different carboxylate anions (formate, propanoate, and butanoate) and a common cation (choline). The values of Δ in formate and propanoate ionic liquids are higher, whereas it is slightly smaller in butanoate than corresponding values in the 175 sodium salts. The work of Tanzi et al.¹⁷⁰ provided vibrational frequencies of these carboxylate anions and assignments on the basis of DFT calculations for isolated ions or ionic pairs and by ab initio MD simulations of clusters of ions. The sequence of calculations for isolated ions, ionic pairs, and clusters highlighted the spectral signature of strong hydrogen bonds between carboxylate anions and the choline cation.

The Raman band shape of the ν(CC) mode is also a probe of the coordinating structure of acetate in solution. Cabaço et al.¹⁶² considered the asymmetry of the ν(CC) Raman band of [C₄C₁im][CH₃COO] at 902 cm⁻¹, which exhibits a high 177 frequency tail due to a low-intensity component at 909 cm⁻¹, as an indication of a fraction of anions in the bidentate coordination. A jointed neutron diffraction and MD simulation study of [C₄C₁im][CH₃COO] by Bowron et al.¹⁷² indeed 178 suggested dominance of unidentate over bidentate coordination of [CH₃COO]⁻ to the hydrogen atoms bonded to the imidazolium ring of [C₄C₁im]. It will be discussed in the next section that an anion hydrogen-bonded to 1-alkyl-3-methylimidazolium cations has significant effect on vibrational frequencies of stretching of C−H ring bonds of the cation. The Raman band at 2917 cm⁻¹ assigned to the ν(CH₂) mode of [CH₃COO]⁻ (see Table 3) overlaps the spectral range of C−H stretching modes of the butyl chain of [C₄C₁im]⁻ (see 179 Figure 19 below).

Vibrations of the trifluoroacetate anion have been discussed by Cabaço et al.¹⁷³. These authors provided a list of vibrational frequencies and assignments for [CF₃COO]⁻ in [C₄C₁im]- [CF₃COO] together with corresponding values for the simple salt Na[CF₃COO] in aqueous solution.¹⁴ Some effects of replacing H by F atoms in going from [CH₃COO]⁻ to [CF₃COO]⁻ are worth noting on the most important vibrations of the anion. In the case of [C₄C₁im][CF₃COO], ν(CH₂) and ν(CH₃) are observed at 1691 and 1406 cm⁻¹, respectively.¹⁷⁴ The difference between them (Δ = 285 cm⁻¹)

Table 4. Assignment According Di

<table>
<thead>
<tr>
<th>#</th>
<th>IR</th>
<th>Raman</th>
<th>assignment</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1021</td>
<td>1021</td>
<td>ref 58; υ(CN₃) + δ(CNC₃) + δ(CH)</td>
</tr>
<tr>
<td>2</td>
<td>1337</td>
<td>1337</td>
<td>ref 58; ν(C(C₂)H₂N) + ν(CN₃) + ν(CH₃)</td>
</tr>
<tr>
<td>3</td>
<td>1378</td>
<td>1385</td>
<td>ref 58; δ(CH₂) + δ(CH₃) + δ(CH₃) + δ(CH₃)</td>
</tr>
<tr>
<td>4</td>
<td>1416</td>
<td>1416</td>
<td>ref 58; ν(CH₃) + δ(CH₃) + δ(CH₃) + δ(CH₃)</td>
</tr>
<tr>
<td>5</td>
<td>1568</td>
<td>1564</td>
<td>ref 58; ν(CH₂) + δ(CH₂) + δ(CH₃) + δ(CH₃) + δ(CH₃)</td>
</tr>
</tbody>
</table>

ν: stretching; δ: in plane bending; w: wagging; r: rocking; s: symmetric; as: antisymmetric; ip: in-phase.

References:
163−166 However, direct comparison with the frequencies observed in ionic liquids is not straightforward since [CH₃COO]⁻ frequencies are very sensitive to coordination. Furthermore, theoretical calculations for [C₄C₁im][CH₃COO] in the gas phase might lead to proton transfer and formation of the N-heterocyclic carbene. This is regarded as an important step along the process of CO₂ absorption, but the theoretical tool employed by Thomas et al.³³ was ab initio molecular dynamics simulation of 36 pairs of [C₄C₁im][CH₃COO] ions, whereas Cabaço et al.¹⁶² performed DFT/B3LYP calculations of a cluster made of two pairs of [C₄C₁im][CH₃COO]⁻[CH₃COO]⁻ ions. In order to identify the CH₃COO⁻ bands, it is useful to compare vibrational spectra of acetate-based and other ionic liquids with the same cation. Cabaço et al.¹³ compared IR and Raman spectra of [C₄C₁im][CH₃COO], [C₄C₁im][BF₄]²⁻, and [C₄C₁im][PF₆]²⁻.

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4.2. Vibrational Frequencies of Cations

4.2.1. Imidazolium. Vibrations of 1-alkyl-3-methylimidazolium cations have been discussed in more detail than other ionic liquid forming cations. Assignment of vibrational frequencies has been done with the help of quantum chemistry calculations for the isolated cation or ion pairs. Berg used MP2 level of theory to calculate vibrational frequencies of [C₄C₁im][BF₄] with two different conformations of the butyl chain. A well-suited level of theory to calculate vibrational frequencies is DFT/B3LYP with a typical basis set, say 6-31+G(d,p). DFT/B3LYP has been used by Dhumal et al. for isolated ions and ion pairs of [C₄C₁im][BF₄] and [Tf₂N]⁺, by Talaty et al. for [C₆C₁im][BF₄] and by Heimer et al. for [C₆C₁im][BF₄]. Once harmonic frequencies follow from these standard calculations, scaling factors are needed for agreement between calculated and experimental data. Grondin et al. calculated harmonic and anharmonic frequencies of [C₄C₁im][BF₄] and [C₆C₁im][BF₄] using the second-order perturbative method proposed by Barone. In order to avoid such scaling factors of harmonic frequencies.

Long tables of vibrational frequencies calculated for 1-alkyl-3-methylimidazolium cations are available in these papers. The composition of normal modes is naturally complicated because of the electronic structure of imidazolium cations. Furthermore, visual inspection of the eigenvectors on computer screen implies that description of the same normal coordinate may vary among different authors. Grondin et al. provided the distribution of potential energy allowing for more rigorous assignment of normal modes in terms of internal coordinates. In the following, we will distinguish three spectral ranges in vibrational spectra of 1-alkyl-3-methylimidazolium cations. The high-frequency range, 2800–3200 cm⁻¹, exhibits a complex pattern of overlapped bands proper to several C–H stretching modes. The 800–1600 cm⁻¹ range includes characteristic bands of imidazolium ring vibrations. The 400–800 cm⁻¹ range, which also contains ring vibrations, is interesting because it provides insight on conformations of alkyl chains. (The low-frequency range probing intermolecular dynamics is the issue of section 5.)

Figure 18 shows IR and Raman spectra in the 1000–1600 cm⁻¹ range of [C₄C₁im][BF₄] (full lines) and [C₄C₁im][CF₃SO₃] (dashed lines) at room temperature. Table 4 gives the assignment of Raman bands marked 1–5.

The stretching of C–H bonds of 1-alkyl-3-methylimidazolium cations can be separated into two groups of bands: 2800–3000 cm⁻¹, belonging to CH modes of alkyl chains attached to the imidazolium ring, and 3000–3200 cm⁻¹, belonging to CH vibrations. The high-frequency range of vibrations of the bands marked 1 and 2 in the Raman spectra of Figure 18.

The stretching of C–H bonds of 1-alkyl-3-methylimidazolium cations can be separated into two groups of bands: 2800–3000 cm⁻¹, belonging to CH modes of alkyl chains attached to the imidazolium ring, and 3000–3200 cm⁻¹, belonging to CH stretching modes. The comparison made in Figure 18 illustrates the well-known finding that this spectral range is a signature of ionic interactions; the imidazolium ring CH stretching modes shift to lower wavenumbers for ionic liquids containing stronger interacting anions. Furthermore, the band at ~3115 cm⁻¹ in the IR spectrum of [C₄C₁im][CF₃SO₃] is much broader than [C₄C₁im][PF₆] and [C₄C₁im][BF₄], suggesting stronger hydrogen bonding in the former. Out-of-plane ring CH vibrations within 700–900 cm⁻¹ are also sensitive to strength of anion–cation interactions, shifting to lower wavenumber with increasing anion basicity.

Using these ρ(CH) vibrations as probes of ionic interactions is better accomplished with IR than Raman spectroscopy because of higher IR activity. Figure 19 also illustrates stronger anion dependence for the ring CH than alkyl CH stretching modes, as expected from the preferred location of anions around the imidazolium polar head. Furthermore, the doubled-peaked feature observed within the 3100–3200 cm⁻¹ range is commonly assigned to stretching of C(2)–H (the low frequency component) and C(4),(5)–H (the high frequency component). This interpretation is supported by quantum chemistry calculations of ionic pair.
imidazolium ring. These findings are considered as evidence in favor of anion–cation hydrogen bonding, the C\(\text{(2)}\)–H···A– arrangement being preferred over C\(\text{(4),(5)}\)–H···A–.

The interpretation of this spectral range in terms of different strengths between C\(\text{(2)}\)–H···A– and C\(\text{(4),(5)}\)–H···A– hydrogen bonds has been disputed by Lassègues et al.\(^{19}\) These authors claim that the double-peaked feature above 3100 cm\(^{-1}\) is instead a Fermi resonance,\(^{15,42}\) resulting from mixing of vibrational states of fundamental CH ring vibrations with overtone and combination bands of ring modes whose fundamental transitions are observed in the 1550–1585 cm\(^{-1}\) range (see Figure 18). Lassègues et al.\(^{59}\) grounded their interpretation by isotopic substitution of each hydrogen atom bonded to the ring in order to clear out the spectral range of 3100–3200 cm\(^{-1}\), leaving the corresponding C–D stretching within the 2300–2400 cm\(^{-1}\) range. In accordance with their proposition, the band at \(~3170\) cm\(^{-1}\) (see Figure 19) includes all C\(\text{(2),(4),(5)}\)–H vibrations, and the band at \(~3115\) cm\(^{-1}\) is overtone and combination bands of ring modes enhanced by Fermi resonance. The alternative assignment put forward by Lassègues et al.\(^{59}\) roused a lively debate in the literature\(^{178,179}\) because it implies there is no need of anion–cation hydrogen bonding to explain the vibrational spectra nor C\(\text{(2)}\)–H being stronger interacting site than C\(\text{(4),(5)}\)–H. Wulf et al.\(^{178}\) strengthened the usual point of view with further quantum chemistry calculations showing that C\(\text{(2)}\)–H modes are always obtained at lower frequency than C\(\text{(4),(5)}\)–H modes in many different ion pairs. However, the cyanate-anions chosen by Wulf et al.\(^{178}\) are strongly interacting species, whereas Lassègues et al.\(^{179}\) provided a reminder that their interpretation concerned imidazolium ionic liquids containing less coordinat- ing anions (e.g., [NTf\(_2\)]\(^{−}\), [BF\(_4\)]\(^{−}\), and [PF\(_6\)]\(^{−}\)). Nevertheless, there is consensus that strongly coordinated anions shift CH stretching modes to lower wavenumber,\(^{178,179,58}\) even though definitive assignment of this spectral range is an open issue in vibrational spectroscopy of imidazolium ionic liquids. Irre- spectively of the assignment of vibrational spectra, yet a more delicate issue is the nature of hydrogen bond between imidazolium cations and anions.\(^{180}\)

Vibrational spectroscopy has been a powerful tool to reveal molecular conformations in ionic liquids. Studies in this direction followed after the discovery of crystal polymorphism in [C\(_4\)C\(_1\)im][Cl] by Hayashi et al.\(^{181}\) and Holbrey et al.\(^{182}\) These authors concluded from X-ray diffraction that [C\(_4\)C\(_1\)im][Cl] forms two crystalline phases differing in the conformation of the butyl chain. Hayashi et al.\(^{181}\) found that these polymorphs exhibit different patterns in the 500–800 cm\(^{-1}\) range of the Raman spectrum, where a group of bands (625, 730, an 790 cm\(^{-1}\)) and (500, 600, an 700 cm\(^{-1}\)) is characteristic of each crystal. All of these bands appear in the Raman spectrum of liquid phase of [C\(_4\)C\(_1\)im][Cl], so that one concludes there is a mixture of conformers in the liquid.\(^{181,183,184}\) Hamaguchi and Ozawa\(^{185}\) reviewed their early Raman spectroscopy studies on conformational changes of [C\(_4\)C\(_1\)im]\(^{+}\) in ionic liquids with Cl\(^{−}\), Br\(^{−}\), I\(^{−}\), [BF\(_4\)]\(^{−}\), and [PF\(_6\)]\(^{−}\). In a previous review, Berg offered a detailed analysis on how alkyl chain conformation of [C\(_4\)C\(_1\)im]\(^{+}\) adds fingerprints in Raman spectra of ionic liquids.\(^{186}\)

We also recommend a very detailed work recently published by Endo et al.\(^{186}\) concerning DFT calculations of conformational flexibility and vibrational frequencies of typical ionic liquid forming cations (imidazolium, pyridinium, pyrrolidinium, and piperidinium). It should be noted that this issue has been addressed mainly by Raman spectroscopy, since features indicating the [C\(_4\)C\(_1\)im]\(^{+}\) conformation are not so evident in the IR spectrum.\(^{99}\) Figure 20 illustrates the frequency range exhibiting bands that characterize anti–anti (AA, 620 and 735 cm\(^{-1}\)) and gauche–anti (GA, 600 and 697 cm\(^{-1}\)) conformations of [C\(_4\)C\(_1\)im]\(^{+}\). Quantum chemistry calculations show that these bands belong to ring deformations coupled to CH\(_2\) rocking motions\(^{3,185}\) so that the actual vibrational frequency is sensitive to the butyl chain conformation. As emphasized by Berg,\(^{147}\) Figure 20 also shows a mixture of gauche and anti conformers in the longer alkyl chain [C\(_6\)C\(_1\)im]\(^{+}\) cation. Kiefer\(^{149}\) and Pye\(^{155}\) considered other bands as signatures of three conformers of [C\(_4\)C\(_1\)im]\(^{+}\) in [C\(_4\)C\(_1\)im][HSO\(_4\)].\(^{1460}\) These authors focused on the anion dependence of relative intensities of the 600 and 620 cm\(^{-1}\) bands. The ratio of intensities \(I_{600}/I_{620}\) increases in the sequence [C\(_4\)C\(_1\)im][I] > [C\(_4\)C\(_1\)im][Br] > [C\(_4\)C\(_1\)im][Cl], so that one concludes that gauche conformation is stabilized for stronger interacting halide anions.\(^{1476}\)

Umebayashi et al.\(^{186}\) and Lassègues et al.\(^{125}\) showed that [C\(_4\)C\(_1\)im]\(^{+}\) conformers with the planar or nonplanar ethyl chain can be distinguished by characteristic bands in the spectral range of 200–500 cm\(^{-1}\) of the Raman spectrum. Figure 21 shows this spectral range of the Raman spectrum of [C\(_4\)C\(_1\)im][Cl] with the bands proposed by these authors as signatures of the [C\(_4\)C\(_1\)im]\(^{+}\) conformation. Endo and Nishikawa\(^{91}\) found
Review

1507 spectra of \([\text{C}_4\text{C}_1\text{im}]\)[\text{NTf}_2]\) and \([\text{C}_4\text{C}_1\text{C}_1\text{im}]\)[\text{NTf}_2]\). Taking 1505 of ionic liquids based on \([\text{C}_1\text{im}]^+\) ring vibrations. Noack et al.196 discussed IR and Raman spectra 1502 tional spectroscopy, the most signifi- 1501 explanations have been proposed. 192
1500 The reason for this e- 1499 \([\text{C}_1\text{im}]^+\) hydrogen bonding, for a given anion the ionic liquid based on 1497 H 1496 leading to \([\text{C}_4\text{C}_1\text{im}]^+\) Methylation at the C (2) position of imidazolium cations, 1493 usage of vibrational spectroscopy for studying phase transition 1491 some bands characterizing mixture of conformers in the liquid 1490 phase are absent in the crystalline phase. Section 6 discusses the 1492 usage of vibrational spectroscopy for studying phase transition 1491 of ionic liquids.
1494 Methylation at the C (2) position of imidazolium cations, 1496 leading to \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\), blocks the most important site for C– 1497 H–A” hydrogen bonding. Despite eliminating this site for 1498 hydrogen bonding, for a given anion the ionic liquid based on 1499 \([\text{C}_4\text{C}_1\text{im}]^+\) is more viscous than the \([\text{C}_4\text{C}_1\text{im}]^+\) counterpart.
1500 The reason for this effect is not fully understood, and different 1501 explanations have been proposed.192–195 Concerning vibra-
1502 tional spectroscopy, the most significant difference between 1503 \([\text{C}_4\text{C}_1\text{im}]^+\) and \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\) is seen in the spectral range of 1504 ring vibrations. Noack et al.196 discussed IR and Raman spectra 1505 of ionic liquids based on \([\text{C}_4\text{C}_1\text{im}]^+\) and \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\), n = 2 and 4, with the \([\text{NTf}_2]^−\) anion. Figure 22 compares vibrational 1507 spectra of \([\text{C}_4\text{C}_1\text{im}]\)[\text{NTf}_2]\) and \([\text{C}_4\text{C}_1\text{C}_1\text{im}]\)[\text{NTf}_2]\). Taking

![Figure 21](image1.png)

**Figure 21.** Raman spectrum of \([\text{C}_4\text{C}_1\text{im}]\)[\text{Cl}] at T = 360 K. Bands marked * belong to the planar conformer, whereas bands marked # belong to the nonplanar conformer.

![Figure 22](image2.png)

**Figure 22.** IR and Raman spectra of \([\text{C}_4\text{C}_1\text{C}_1\text{im}]\)[\text{NTf}_2]\) (green and blue lines) and \([\text{C}_4\text{C}_1\text{im}]\)[\text{NTf}_2]\) (red and black lines) at room temperature. The bands marked with asterisk is assigned to an anion normal mode. Bands marked with arrows (Raman, 1515 cm\(^{-1}\); IR, 1540 cm\(^{-1}\)) belonging to \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\) have the atomic displacements of the corresponding normal modes shown in Figure 23.

displacements calculated in this work at the DFT/B3LYP 1511 level of theory for two normal modes given new spectral 1512 features in IR (1540 cm\(^{-1}\)) and Raman (1515 cm\(^{-1}\)) spectra of 1513 \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\)[\text{NTf}_2]\). The small mass of hydrogen implies large 1514 displacements of hydrogen atoms in the eigenvectors displayed 1515 in Figure 23. However, in terms of potential energy distribution 1516 calculated with the VEDA program,50 the \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\) IR 1517 band at 1540 cm\(^{-1}\) involves mainly stretching of N(1)–C(2) and 1518 N(3)–C(2) bonds (29%) and bending of the methyl group and 1519 the C(3)–N(3)–C(2) angle (23%). The Raman band at 1515 1520 cm\(^{-1}\) involves stretching of C(2)–CH₃, C(4)–CH₃ (5), and N(1)– 1521 C(2) bonds (54%) and bending of the N(1)–C(2)–N(3) angle 1522 (13%). Hunt et al.197 showed that the electronic structure of 1523 imidazolium cations is better represented by the double bond 1524 C(2)=C(3) and delocalization in the N(1)–C(2)–N(3) bonds of the 1525 ring.197 Therefore, the 1515 cm\(^{-1}\) Raman band of 1526 \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\) is very intense because of vibrations of N(1)– 1527 C(2)–N(3) and C(2)=CH₃ moieties with large polarizability 1528 fluctuation. Endo et al.198 discussed the effect of methylation of 1529 the C(2) position on the spectral ranges of C–H stretching 1530 modes and 550–800 cm\(^{-1}\). Raman frequencies of C(4)(5)=H 1531 stretching modes change when \([\text{C}_4\text{C}_1\text{im}]^+\) is replaced by 1532 \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\), shifting to lower wavenumber when the counterion is Cl\(^-\), Br\(^-\), or I\(^-\), but shifting to a higher 1533 wavenumber when the counterion is [BF₄]\(^-\) or [PF₆]\(^-\). The 1534 relative intensities of bands that characterize AA and GA 1535 conformers (see previous Figure 20) change in going from 1537 \([\text{C}_4\text{C}_1\text{im}]^+\) to \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\). These findings were considered as the 1538 consequence of the local arrangement of anions around 1539 \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\) being different from \([\text{C}_4\text{C}_1\text{im}]^+\).198

Fewer works have been dedicated to detailed assignment of 1541 vibrational frequencies of proton imidazolium ionic liquids (i.e., 1542 monooalkylimidazolium with a free N–H bond). Moschovi et al.118 discussed IR and Raman spectra as a function of 1544 temperature of \([\text{C}_1\text{im}]^+\)[\text{NTf}_2]\), which melts at 325 K, where 1545 \([\text{C}_1\text{im}]^+\) is the 1-H-3-methylimidazolium cation. Moschovi et al.118 addressed the issue of vibrational signatures of \([\text{NTf}_2]^−\) and 1547 conformers and the effect of the hydrogen bond on the N–H 1548 and C–H vibrations of the imidazolium ring. This work 1549 provides full tables of observed IR and Raman frequencies and 1550 vibrational assignments for \([\text{C}_1\text{im}]^+\)[\text{NTf}_2]\). An expected differ-
1551 ence in comparison with 1,3-dialkylimidazolium cations is the 1552 occurrence of the N–H stretching mode of \([\text{C}_1\text{im}]^+\) at higher 1553

![Figure 23](image3.png)

**Figure 23.** Atomic displacement of the two normal modes of \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\) calculated at the DFT/B3LYP level of theory for the isolated cation. The harmonic vibrational frequencies calculated at 1533 and 1560 cm\(^{-1}\) correspond to experimental bands at 1515 and 1540 cm\(^{-1}\), respectively, of \([\text{C}_4\text{C}_1\text{C}_1\text{im}]^+\)[\text{NTf}_2]\) (bands marked by arrows in Figure 22).
frequency than the C–H stretching modes. The ν(N–H) mode is observed at 3287 cm⁻¹ in the Raman spectrum of solid [C₄im][NTf₂], becoming a very weak band at 3281 cm⁻¹ upon melting. The ν(N–H) mode gives intense IR bands both in solid and liquid phases of [C₄im][NTf₂], 3271 and 3273 cm⁻¹, respectively, although broader in the liquid.¹¹¹ Moschovi et al.¹¹⁹ went further in reporting IR and Raman spectra for a series of protic ionic liquids [C₈im][NTf₂], n = 0–12. Insights on conformation of the alkyl chain of [C₈im]⁺ cations have been obtained from the Raman bands in the 820–900 cm⁻¹ range, corresponding to deformation motions of the CH₃ group at the end of the chain.¹¹⁶ It has been found that vibrational frequencies of N–H and C–H stretching modes in protic [C₄im][NTf₂] and also C–H modes in nonprotic [C₈im][NTf₂],¹²⁰ decrease as n increases, but these findings have not been considered as signatures of stronger anion–cation hydrogen bonding. These authors considered instead the role played by an intramolecular effect, that is, the positive charge on the imidazolium ring is diminished by the electron donor inductive effect of longer alkyl chain, so that the strength of anion–cation interaction does not increase even though polar/nonpolar segregation becomes better defined in ionic liquids with the imidazolium cation of the long chain. In a subsequent work, Moschovi et al.¹²¹ provided very detailed analyses and comparisons of vibrational spectra for nonprotic, [C₄,C₈im][NTf₂], and protic, [C₄im][NTf₂], ionic liquids.

Inserting a functional group in the side chain of 1-alkyl-3-methylimidazolium cations might result in ionic liquids with improved properties for some specific tasks (e.g., gas absorption). Despite vibrational spectroscopy being a powerful tool to characterize molecular interactions in these solutions (see section 7), detailed spectroscopic analyses and assignments of vibrations for these imidazolium derivatives are more sparse than the usual 1-alkyl-3-methylimidazolium cations. Once the vibrational frequencies of [C₄,C₈im]⁺ and anions are well-established, the most important band of the added functional group is easily identified. Figure 24 shows molecular structures of some derivatives whose characteristic vibrations we show in Figure 25.

Figure 24. Molecular structures of some functionalized imidazolium cations.

Xuan et al.²⁰² studied 1-allyl-3-methylimidazolium dicyanamide and 1-allyl-3-methylimidazolium chloride with assignments based on potential energy distributions of normal modes calculated for ion pairs at the DFT/B3LYP level of theory. Figure 25A shows IR and Raman spectra of 1-allyl-3-methylimidazolium dicyanamide in the spectral range where the C=C stretching mode is observed at 1647 cm⁻¹ in the Raman spectrum. Xu et al.²⁰³ assigned a few IR bands of 1-allyl-3-methylimidazolium bicarbonate in agreement with the more complete assignment of ref 202. The quantum chemistry calculations of Xuan et al.²⁰² indicated three stable conformers of the 1-allyl-3-methylimidazolium cation, but no spectroscopic signatures have been proposed for these conformers. Shirotta et al.²⁰⁴ discussed the vibrational spectra of some ionic liquids containing benzyl-substituted cations, and Xue et al.²⁰⁵ compared the spectra of 1-benzyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) and a solution of benzene in [C₈,C₈im][NTf₂]. However, these works focused on the low-frequency range obtained by femtosecond Raman-induced Kerr effect spectroscopy. Shirotta et al.²⁰⁴ provided the observed vibrational frequencies for bands below 700 cm⁻¹, and they distinguished the vibrations belonging to anions or cations. We show in Figure 25B part of the vibrational spectra, including the most characteristic new feature of 1-benzyl-3-methylimidazolium dicyanamide. The sharp band observed at 1003 cm⁻¹ in the Raman spectrum of the ionic liquid is the counterpart to the totally symmetric breathing mode of benzene.

There is still no detailed analysis of vibrational spectra of an ionic liquid based on CN-functionalized imidazolium cation. Figure 25C shows the characteristic band of the CN stretching vibration in 1-(3-cyanopropyl)-3-methylimidazolium bis(trifluoromethanesulfonylimide), [NC-C₃(C₃)im][NTf₂], at room temperature. The vibrational frequency of the ν(CN) mode at 2251 cm⁻¹ in [NC-C₃(C₃)im][NTf₂] lies at a significantly higher wavenumber than cyanate-anions (see Figure 10 and Table 1). The ν(CN) frequency in [NC-C₃(C₃)im][NTf₂] is indeed close to the value in the molecular liquid acetonitrile (2253 cm⁻¹).

Knorr et al.²⁰⁶,²⁰⁷ discussed temperature effect on the IR band corresponding to O–H stretching mode of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, [HO-C₂C₃im][BF₄]. The ν(OH) spectral range is shown in Figure 25D for [HO-C₂C₃im][BF₄] at room temperature, where the strong feature at ∼3552 cm⁻¹ in the IR spectrum belongs to the O–H stretching motion in O–H–F hydrogen bonded to [BF₄]⁻. Knorr et al.²⁰⁶,²⁰⁷ found that the low-frequency tail in the IR band grows in intensity with decreasing temperature, becoming a well-resolved band at ∼3402 cm⁻¹ at 233 K. With the support of quantum chemistry calculations of clusters of...
ions, this low-frequency component has been assigned to the O–H vibration engaged in O–H–O hydrogen bond with the neighbor cation.206,207 Katsuya et al.208 observed a weak band at ~3425 cm⁻¹ in the IR spectrum of [HO-C₆H₄C₆H₃][PF₆] and they also assigned it to υ(OH) in hydrogen bonding with –OH groups of neighbor cations. Hydrogen bonding between like-charge species has also been suggested for the choline cation from the analysis of the O–H stretching region of IR spectra of [Cho][NTf₂].209 Knorr et al.200,207,209 pointed out that these are the first spectroscopic evidence of what Weinhold and Klein210 called an antielectrostatic hydrogen bond (i.e., a hydrogen bond between ions of the same charge). It is worth remembering, however, that signature of anion–anion hydrogen bond between [HSO₄]⁻, previously found in IR and Raman spectra of crystals of the halide salts, and by Zheng et al.,216 discussed IR and Raman for the [C₄C₃im][HSO₄] and [C₆C₅im][HSO₄] as discussed in the previous section.

4.2.2. Pyridinium. Gale et al. discussed Raman211 and IR212 spectra of N-butylpyridinium in the early period of room temperature molten salts based on mixtures of an organic cation chloride and AlCl₃. Tait and Osteryoung213 found that the main difference in IR spectra between basic and acidic AlCl₃/N-butylpyridinium chloride mixtures (acidic melts have AlCl₃:organic salt mole ratio greater than 1) occurs in the C–H stretching region, in particular enhancement in the intensity of bands of aliphatic relative to aromatic C–H stretching modes.

Tables of experimental frequencies of cation vibrations are available;213 however, the most important issue of a vibrational spectroscopy study of those systems was identifying complex cation normal modes.214,215 Figure 26 shows the fingerprint regions of IR and Raman spectra of 1-butyl-4-methylpyridinium bromide, [Py₁₄⁺Br], and 1-butyl-4-methylpyridinium tetrafluoroborate, [Py₁₄⁺BF₄], at room temperature. Bands marked with asterisk belong to anion vibrations. For comparison purposes, IR and Raman spectra of solid [Py₁₄⁺Br] are shown by green and blue lines, respectively.

Figure 26. IR (red) and Raman (black) spectra of 1-butyl-4-methylpyridinium tetrafluoroborate, [Py₁₄⁺BF₄], at room temperature. Bands marked with asterisk belong to anion vibrations. For comparison purposes, IR and Raman spectra of solid [Py₁₄⁺Br] are shown by green and blue lines, respectively.

Figure 27. Raman spectra of liquid [Py₁₄⁺][BF₄] (black line) and solid [Py₁₄⁺][Br] (blue line) at room temperature in the region including bands assigned to different [Py₁₄⁺⁺] conformers. Vibrational frequencies and relative intensities calculated for [Py₁₄⁺⁺] are indicated by green (886 cm⁻¹, gauche) and red (917 cm⁻¹, anti) lines. Atomic displacement vectors calculated for these normal modes are shown for each conformer.

Raman bands (887 and 909 cm⁻¹ in liquid [Py₁₄⁺][BF₄]; 892 and 913 cm⁻¹ in solid [Py₁₄⁺][Br]) that can be used to discriminate each conformer. These bands correspond to Raman active modes with frequencies calculated at 886 and 917 cm⁻¹, respectively, for gauche and anti [Py₁₄⁺⁺] conformers. Figure 27 highlights this spectral range of the Raman spectra of [Py₁₄⁺][BF₄] and [Py₁₄⁺][Br] together with peak position and relative Raman intensities obtained from the DFT calculation. This figure indicates there is a mixture of gauche and anti [Py₁₄⁺⁺] conformers in both solid [Py₁₄⁺][Br] and liquid [Py₁₄⁺][BF₄]. Recently, Endo et al.186 provided a detailed theoretical analysis by DFT calculations on the conformational flexibility and the corresponding vibrational frequencies of the most common organic cations forming ionic liquids. In the case of pyridinium derivatives, the calculations suggest that the 480–510 and 740–820 cm⁻¹ regions of the Raman spectrum could also be used to identify different conformers.

4.2.3. Pyrrolidinium. The relationship between vibrational frequency and molecular conformation has been studied in more detail for 1,1-dialkylpyrroldinium than pyrrolidinium cations. Castriota et al.114 reported Raman spectra in the 250–1700 cm⁻¹ range of ionic liquids based on 1-methyl-1.
propyliopyridinium, [Pyr$_{1,4}$]$^+$, with the anions [NTf$_2$]$^−$ and I$^−$. However, assignment of [Pyr$_{1,4}$]$^+$ vibrations was not given because the issue was coordination of Li$^+$ by [NTf$_2$]$^−$ in a 2:1 mixture of [Pyr$_{1,4}$][NTf$_2$] with Li[NTf$_2$]. The analogous effect of a strong polarizing cation on the [NTf$_2$]$^−$ vibrations has been discussed by Rocher et al. in [Pyr$_{1,4}$][NTf$_2$]/AlCl$_3$ mixtures as a function of Al$^{3+}$ concentration. The clear signature provided by Raman spectroscopy about coordination of [NTf$_2$]$^−$ to Li$^+$ will be discussed in section 7. The vibrational motions of [Pyr$_{1,4}$]$^+$ and [Pyr$_{1,4}$]$^+$ have been discussed in several works. Besides gauche or anti conformation of the butyl chain, additional issues concerning [Pyr$_{1,4}$]$^+$ include equatorial or axial position (eq or ax) of the butyl chain relative to ring carbon atoms, and envelope or twist conformation of the nonplanar ring. By comparing experimental Raman spectrum and DFT/B3LYP calculation within the whole 200−1600 cm$^{−1}$ range, Fujimori et al. concluded that in [Pyr$_{1,4}$][NTf$_2$] the butyl chain and the ring are at all anti and envelope conformations, respectively, but there is mixture of eq and ax [Pyr$_{1,4}$]$^+$ conformers. It is difficult to characterize the conformers when many experimental and calculated frequencies have to be compared, instead of a small frequency range including a few characteristics bands. Comparison with related systems with a single conformer in crystalline phase (e.g., [Pyr$_{1,4}$]Br) helps identifying appropriate bands as the fingerprint of a given conformer. Bands observed at 486, 586, and 655 cm$^{−1}$ in the Raman spectrum of solid [Pyr$_{1,4}$]Br closely match the frequencies calculated for [Pyr$_{1,4}$]$^+$ in ax−anti-envelope conformation. Figure 28 shows IR and Raman spectra of [Pyr$_{1,4}$][NTf$_2$] in the range of 860−950 cm$^{−1}$ used by Fujimori et al. in order to reveal coexisting eq and ax [Pyr$_{1,4}$]$^+$ conformers in the liquid phase. Although there is overlap of bands in this region, quantum chemistry calculations indicate that the 883 cm$^{−1}$ Raman band is a signature of the ax conformer, whereas the 890−930 cm$^{−1}$ range includes bands of both eq and ax conformers. Furthermore, the intensities of components at 892, 905, and 930 cm$^{−1}$ decreases with increasing temperature, while the intensity of the 883 cm$^{−1}$ band remains the same, also indicating a mixture of eq and ax [Pyr$_{1,4}$]$^+$ conformers in [Pyr$_{1,4}$][NTf$_2$]. Umeyashiki et al. also concluded for mixtures of eq and ax conformers in [Pyr$_{1,4}$][NTf$_2$] and [Pyr$_{1,4}$][NTf$_2$] on the basis of the DFT/B3LYP calculations and the temperature dependence of Raman spectra in the range shown in Figure 28. Fujii et al. paid attention to the 250−400 cm$^{−1}$ range of the Raman spectrum of [Pyr$_{1,3}$][N(SO$_2$F)$_2$], in which cation bands at 350 and 380 cm$^{−1}$ again indicate a mixture of [Pyr$_{1,3}$]$^+$ conformers. There is an interesting contrast between these studies on pyrroliinium and imidazolium ionic liquids: there is mixture of anti and gauche conformation of the butyl chain in [C$_4$C$_1$im]$^+$ ionic liquids, but anti conformation of [Pyr$_{1,3}$]$^+$ predominates with negligible population of the gauche conformer. However, when [Pyr$_{1,4}$]$^+$ is functionalized upon insertion of an ether group function in the long alky chain then IR spectroscopy with support of DFT calculations indicate that the side chain acquires gauche geometry. A distinctive aspect of works by Vitucci et al. and Mao et al. is that these authors considered the IR spectrum, rather than the Raman spectrum, of [Pyr$_{1,4}$][NTf$_2$]. In order to assign the IR bands by DFT calculations, Vitucci et al. considered the isolated ion, whereas Mao et al. considered an ionic pair. Tables containing assignment of [Pyr$_{1,4}$]$^+$ frequencies are available. In particular, Figure 6 of ref 121 provides visualization of atomic displacements for the normal modes corresponding to the bands shown in Figure 28.

### 4.2.4. Piperidinium.

Derivatives of piperidinium encompass an important class of ionic liquid forming cations, but assignment of vibrational spectra has been much less discussed for piperidinium than imidazolium or pyrrolidinium cations. Shukla et al. compared calculated and experimental IR and Raman spectra of N-butyl-N-methylpiperidinium bis(trifluoromethanesulfonylimide, [Pip$_{1,4}$][NTf$_2$] and [Pip$_{1,4}$]Br, the latter being a solid with a relatively high melting point (241 °C). Figure 29 shows IR and Raman spectra of [Pip$_{1,4}$][NTf$_2$] and [Pip$_{1,4}$]Br. As the [NTf$_2$]$^−$ bands dominate the spectra of [Pip$_{1,4}$][NTf$_2$], we provide spectra for solid [Pip$_{1,4}$]Br in order to...
1796 to highlight the [Pip1,4]+ bands. Conformations of piperidinium cations, including ring flexibility (chair, 1797 twist, or boat), eq or ax position of the butyl chain, and 1798 rotational isomers of the butyl chain. The DFT/B3LYP 1799 calculations of Shukla et al.120 indicated that the more stable 1800 conformation is chair for the piperidinium ring and gauche for 1801 the butyl chain. The characteristic Raman bands of cisoid and 1802 transoid conformations of [NTf2]− were discussed by Shukla et 1803 al.,120 but they did not identify vibrations that could be used as 1804 signatures of cation conformation. Shimizu et al.132 identified 1805 characteristic bands of [Pip1,4]+ conformers in the range of 1806 700–800 cm−1 of the Raman spectrum of [Pip1,4][N(SO2F)2]. 1807 With the support of DFT/B3LYP calculations for the chair 1808 form of [Pip1,4]+, Shimizu et al.132 proposed that eq and ax 1809 conformations of [Pip1,4] can be identified by the Raman 1810 bands at 704 and 710 cm−1, respectively, in the crystalline 1811 phases of [Pip1,4][N(SO2F)2]. In the liquid phase, the Raman 1812 spectrum indicates a mixture of eq and ax conformers of 1813 [Pip1,4]−.

4.2.5. Ammonium. A large variety of ionic liquids can be 1814 prepared from mono-, bi-, tri-, and tetraalkylammonium 1815 cations, [C1C1C1C3N]+, [C1C1C1C6N]+, [C1C1C1C3N]+, and 1816 [C1C1C1C6N]+, respectively, with lengths of alkyl chains 1817 indicated by the number of carbon atoms i, j, k, and l. 1818 Vibrational frequencies of the prototype [NH4]+ of Td 1819 symmetry in halide salts were already reviewed by Herzberg.42 1820 3033 (a vibration mixing C−H bending modes, and the 1821 H bending modes, and the 1822 1550 cm−1 range of the IR spectrum 1823 −methyl- 1824 −methyl- 1825 1,350–1550 cm−1 corresponds to C−H bending modes, and the 1826 range of 800–1550 cm−1 corresponds to normal modes with 1827 displacements of many atoms of the cation. The complex 1828 patterns of atomic displacements calculated for the normal 1829 modes of [C1C1C1C3N]+ and [C1C1C1C6N]+ can be found in 1830 ref 121. In a subsequent work, Vitucci et al.122 discussed 1831 spectral changes after crystallization of [C1C1C1C3N][NTf2] 1832 and [C1C1C1C6N][NTf2] at ~250 K.

The possibility of revealing alkyl chain conformation of 1835 tetraalkylammonium cations by combined usage of IR spec- 1836 troscopy and quantum chemistry calculations is a more 1837 challenging task in comparison with the above discussion on 1838 1-alkyl-3-methylimidazolium cations. Palumbo et al.223 used the 1839 DFT/B3LYP level of theory to calculate vibrational frequencies 1840 for six different conformers of [C1C1C1C3N]+. An appropriate 1841 spectral window for comparison between calculation and 1842 experiment is the 900–1070 cm−1 range of the IR spectrum 1843 of [C1C1C1C3N][NTf2]. The calculations indicated that the IR 1844 feature at 1000 cm−1 (a vibration mixing C−C, C−N 1845 stretching, and CH3 wagging) is a characteristic band of the 1846 lowest energy [C1C1C1C3N]+ conformer.223 Occurrence of 1847 several bands in this spectral range indicates a mixture of 1848 conformers in the liquid phase, whereas only the lowest-energy 1849 conformer is retained in the crystalline phase accompanied by 1850 concomitant change in the spectral pattern.223 The application 1851 of vibrational spectroscopy to investigate phase transitions of 1852 ionic liquids will be reviewed in section 6.

Domanska and Bogel- Lukasik,224 in a study focusing on 1853 thermodynamic properties of ammonium salts, provided the IR 1854 frequencies of solid phases of tetraalkylammonium bromide 1855 salts in which one of the alkyl chains has been functionalized 1856 with a terminal −OH group. Aparicio et al.225 used the high- 1857 frequency range of the IR spectrum, 3100–3600 cm−1, in order 1858 to monitor water uptake from the atmosphere by ionic liquids 1859 based on 2-hydroxyethyltrimethylammonium and tris(2- 1860 hydroxyethyl)methylammonium cations, but detailed assign- 1861 ment of cation vibrations was not an issue. A discussion on the 1862 nature of vibrations was given by Arkas et al.226 for N,N-di(2- 1863 hydroxyethyl)-N-methyl-N-alkylammonium bromides (alkyl 1864 chain from dodecyl to octadecyl), however, within the context 1865 of liquid-crystal phase transition.

Concerning −OH-functionalized ammonium cations, more 1866 detailed spectroscopy studies have been reported for choline 1867 (i.e., hydroxyethyltrimethylammonium, [Cho]+). In the case of 1868 nonprotic tetraalkylammonium ionic liquids, an indication of 1869 weak interaction comes from finding that simple juxtaposition 1870 of vibrational frequencies calculated for isolated anion and 1871 cation give reasonable agreement to experimental spectra.121 1872 On the other hand, this is not the expectation for systems with 1873 the possibility of strong hydrogen bonds such as choline cation 1874 with carboxylate170 or amino acid anions.175 Vibrational 1875 1021/acs.chemrev.6b00461

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frequencies of the choline cation have been discussed by Tanzi et al. in ionic liquids with formate, propanoate, or butanoate. By comparing quantum chemistry calculations for the isolated choline and the choline–anion pair, these authors found the expected hydrogen bond induced frequency shift: $\nu$(OH) shifts to a lower wavenumber, whereas HOC bending and CO stretching and torsion modes shift to a higher wavenumber. The more powerful tool to calculate vibrational spectra of these strongly hydrogen-bonded ionic liquids is ab initio MD simulation, since the method takes into account many different ionic arrangements resulting from the liquid dynamics. Tanzi et al. showed that Raman spectra of choline carboxylates exhibit a large variability of O–H stretching frequencies within 3200–3400 cm$^{-1}$, whereas the less perturbed C–H stretching modes of choline cover narrower range centered at ~2985 cm$^{-1}$. This spectral separation between O–H and C–H stretching modes is clear in IR spectra reported by Harmon et al. for the simple salts choline bromide and choline iodide. The O–H stretching band in the IR spectrum of [Cho][NTf$_2$] exhibits a tail with components at 3431 and 3474 cm$^{-1}$ which have been assigned as the signature of hydrogen bonding between neighboring choline cations. On the other hand, the IR spectrum reported by Campetella et al. for choline with the amino acid alanine anion alanine, where there is also overlap with the alanine N–H stretching modes, shows a broad band covering the whole 2500–3500 cm$^{-1}$ range. The environmental-induced modifications of IR spectra have also been discussed by Perkins et al. for the eutectic mixture of choline chloride and urea (1:2 molar ratio). The $\nu$(OH) IR band in pure choline chloride is a relatively sharp band at 3256 cm$^{-1}$, which overlaps the N–H stretching modes of urea upon formation of the mixture. It is difficult to correlate vibrational frequencies in the spectral range of 700–1700 cm$^{-1}$ for simple choline halides with the frequencies observed in ionic liquids with strongly interacting carboxilate and amino acid anions. For instance, the IR band at 1088 cm$^{-1}$ for choline carboxylate, which agrees with the value for choline halides, was assigned to the choline CO stretching mode in ref 170, but the corresponding band at 1091 cm$^{-1}$ in choline alanine was assigned to CH rock and twisting. Thus, it would be interesting to mark the choline vibrational frequencies in IR and Raman spectra of an ionic liquid with a less interacting anion. Once the [NTf$_2$]$^-$ frequencies were already discussed in the previous section, then we show IR and Raman spectra of [Cho][NTf$_2$] in Figure 31 with the choline bands indicated by arrows. Harmon et al. assigned the choline normal modes within 700–2000 cm$^{-1}$, assuming a C$_3$ point group for the (CH$_3$)$_2$N–CH$_2$– moiety. Some of the IR frequencies reported for choline halides have a correspondent feature in the spectra shown in Figure 31 for [Cho][NTf$_2$]. The first example of the series of protic alkylammonium ionic liquids is monomethylammonium, [C$_4$NH$_3$]$^+$. Raman spectra and X-ray powder diffraction as a function of temperature have been reported by Bodo et al. for [C$_4$NH$_3$][NO$_3$], which melts at 381 K. Calculation of vibrational spectra have been done by first using classical MD simulation of clusters of ion pairs, ([C$_4$NH$_3$][NO$_3$])$_n$ u to 8, in order to generate reasonable configurations, which were then optimized by quantum chemistry calculation at the DFT/B3LYP level of theory. This approach aims for a better representation of the hydrogen bond network and the condensed phase spectrum. The high-frequency range of the Raman spectrum of liquid [C$_4$NH$_3$][NO$_3$]. Several groups of Raman bands were assigned to [C$_4$NH$_3$]$^+$ vibrations: $\nu$(C=$\equiv$N) bending (416–450 cm$^{-1}$), $\nu$(C–N) symmetric stretching (780–890 cm$^{-1}$), CH$_3$ and CH$_2$ wagging ($\sim$990 cm$^{-1}$), asymmetric C=C and C=N stretching ($\sim$950 cm$^{-1}$), C$_2$ rocking (1175–1195 cm$^{-1}$), CH$_3$ scissoring ($\sim$1300 cm$^{-1}$), and CH$_2$ and CH$_3$ bending (1450–1460 cm$^{-1}$).
A specific comment concerns the band located at 870−890 cm$^{-1}$, which Henderson et al.$^{232}$ assigned instead to C−C stretching and found at 875 cm$^{-1}$ in the Raman spectrum of $[C_2NH_3][NO_3]$. This assignment is in line with a detailed analysis performed by Hagemann and Bill$^{233}$ of the Raman spectra of the simpler salts $[C_2NH_3]Cl$ and $[C_2NH_3]Br$. These authors provided a full list of Raman frequencies and assignments for ethylammonium halides, including the complicated pattern of bands intensified by Fermi resonance in the high-frequency range of C−H and N−H stretching modes. It is worth mentioning that the $\nu$(CC) mode at 1047 cm$^{-1}$ in $[C_2NH_3]Cl$ is an useful probe of local structure along the phase transition,$^{232,234}$ but it is hidden by the intense anion band $\nu$(NO$_3$) in $[C_2NH_3][NO_3]$. Nevertheless, there is nice agreement between experiment and theory,$^{241}$ in particular the finding that cation frequencies within 400−1700 cm$^{-1}$ depend on the alkyl chain length of $[C_2NH_3]$.

Faria et al.$^{235}$ calculated vibrational frequencies for different conformers of $[C_2NH_3]^+$ at the DFT/B3LYP level of theory. Temperature and pressure-induced crystallization of $[C_2NH_3]_2[NO_3]$ helped Faria et al.$^{235}$ to propose that Raman bands at 828 and 868 cm$^{-1}$ characterize, respectively, gauche and anti conformers of $[C_2NH_3]^+$ (i.e., there is a mixture of conformers in the liquid phase of $[C_2NH_3][NO_3]$) (see Figure 32). The high-frequency spectral range, which is separated into bands belonging to C−H and N−H stretching modes, is barely affected by the alkyl chain length because hydrogen bonds remain essentially the same between the polar head of $[C_2NH_3]$ and the nitrate anion.$^{231}$ Bodo et al.$^{236}$ have also compared the experimental Raman spectrum of liquid $[C_2NH_3][NO_3]$ with the power spectrum obtained from the Fourier transform of the time correlation function of atomic velocities calculated by ab initio MD simulation. IR frequencies have been reported by Luo et al.$^{237}$ for derivatives containing longer alkyl chains (trioctylammonium) and the more complex triphenylammonium (and also the trialkylphosphonium counterpart) triflate ionic liquids.

4.2.6. Other Cations. In Berg's review on Raman spectroscopy of ionic liquids,$^3$ he provided preliminary results for a system based on the tetramethylguanidinium cation, $[\text{TMGH}]^+$. More detailed analysis of vibrations of $[\text{TMGH}]^+$ have been performed by Berg et al.$^{238}$ and Horikawa et al.$^{239}$ for $[\text{TMGH}][\text{NTf}_2]$, and by Berg et al. for $[\text{TMGH}][\text{Cl}]$ and $[\text{TMGH}][\text{Br}]$. These works provide lists of vibrational frequencies experimentally observed and calculated by quantum chemistry methods.

Carper et al.$^{242}$ reported IR and Raman spectra of trimethylsulfonium dicyanamide, $[\text{C}_3\text{C}_2\text{S}][\text{N(CN)}_2]$. The authors provided vibrational assignment based on quantum chemistry calculations for an ionic pair and a dimer $([\text{C}_3\text{C}_2\text{S}][\text{N(CN)}_2])_2$. We show in Figure 33 the fingerprint range of IR and Raman spectra of other alkylsulfonium ionic liquids, $[\text{C}_2\text{C}_2\text{S}][\text{NTf}_2]$, with some cation bands indicated by arrows.

4.3. Applications

The discussion of vibrational frequencies and normal modes assignments for important anions and cations in the previous sections already stated some of the applications of vibrational spectroscopy in studies of ionic liquids. This section aims an overall view of these and further applications of vibrational spectroscopy of pure ionic liquids.

One of the most fundamental applications of molecular spectroscopy$^{14}$ is the calculation of thermodynamic properties$^{20}$ of the ideal polyatomic gas model, for which exact expressions exist for the partition function of translational, rotational, and vibrational degrees of freedom. Focusing here on the vibrational contribution, the knowledge of vibrational frequencies allows for the calculation of thermodynamic functions according to fundamental expressions of statistical mechanics (e.g., for the heat capacity of harmonic oscillators):$^{74,243}$

$$
\frac{C_v}{Nk} = \sum_{j=1}^{3N-6} \left( \frac{h\nu_j}{kT} \right)^2 \frac{e^{h\nu_j/kT}}{(e^{h\nu_j/kT} - 1)^2}
$$

where $k$ is the Boltzmann constant, $\hbar$ is the Planck constant, $T$ is temperature, $N$ is the number of atoms, and the summation extends to the $3N-6$ normal modes $(3N-5$ for linear molecules) each one with vibrational frequency $\nu_j$. Paulecha et al.$^{244}$ calculated heat capacity, energy, and entropy for the ideal gas phase of $[\text{C}_2\text{C}_1\text{im}]\text{[PF}_6]$.$^{245}$ Blokhin et al.$^{246}$ calculated these thermodynamic properties for $[\text{C}_2\text{C}_1\text{im}]\text{[NTf}_2]$,$^{247}$ and Paulecha et al.$^{248}$ extended the calculations for the series $[\text{C}_2\text{C}_1\text{im}]$−$[\text{NTf}_2]$, $n = 2, 4, 6,$ and 8. Following a combined usage of experimental IR frequencies and calculated by quantum chemistry methods, these works give full lists of vibrational frequencies $\nu_j$ that have actually been considered in the thermodynamic calculations. Some low frequencies are not included in the summation because they correspond to internal rotations, which are commonly represented by an empirical cosine potential function for hindered rotations.$^{74,243}$ Rotational contributions to thermodynamic properties take into account the moments of inertia given in these works.$^{244-246}$

The quantum chemistry calculations giving the full set of vibrational frequencies needed in evaluating thermodynamic properties have been done for a cation−anion pair because it is considered that the gas phase of ionic liquids is made of ion pairs rather than isolated ions.$^{247,248}$ Dong et al.$^{249}$ were able to obtain in situ IR spectrum of $[\text{C}_2\text{C}_1\text{im}]\text{[NTf}_2]$ in gas phase after vacuum distillation of the liquid at $150 \, ^\circ\text{C}$. Relative intensities of some bands change in the gas phase in comparison with the liquid phase spectrum, a finding$^{249}$ reproduced by calculations of IR spectra of clusters of different sizes.$^{249}$ Obi et al.$^{250}$ and Cooper et al.$^{251}$ also concluded for vaporization of $[\text{C}_2\text{C}_1\text{im}]\text{[NTf}_2]$ as ion pairs, but these workers$^{252}$ obtained the IR spectrum after trapping the vapor in helium nanodroplets at very low temperature$^{253}$ or supersonic jet. 

![Figure 33. IR (red, transmittance scale at right) and Raman (black) spectra of $[\text{C}_2\text{C}_2\text{S}][\text{NTf}_2]$ at room temperature. Some bands assigned to $[\text{C}_2\text{C}_2\text{S}]^+$ are indicated by arrows.](image-url)
cooled in helium carrier gas. The role played by methylation of the imidazolium ring on the strength of interactions of the anion to the imidazolium cation was addressed by Fournier et al., who compared IR spectra of \([\text{C}_4\text{C}_1\text{im}][\text{BF}_4]\) and \([\text{C}_4\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]\). Both trapping techniques of helium nanodroplets and matrix isolation were used by Hanke et al.,

to reveal individual ion contributions to the IR spectra of \([\text{C}_4\text{C}_1\text{C}_6\text{im}][\text{NTf}_2]\). Booth et al. identified in the gas phase several conformers of \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\) ion pairs with different strengths of interaction with the anion according to the magnitude of vibrational frequency shift of the \(C(2)-H\) stretching mode. Berg et al. obtained in situ gas phase Raman spectrum of a protic ionic liquid, 1-methylimidazolium acetate. Comparison between spectra of the gas phase ion liquid and 1-methylimidazolide and acetic acid indicated that proton transfer takes place upon vaporization, so that the gas phase of this protic ionic liquid is made of the starting neutral molecules. However, this is not a general rule for protic ionic liquids as demonstrated by Horikawa et al., who obtained IR spectra of several protic ionic liquids after vaporization and trapping in a cryogenic neon matrix. Comparison between spectra of the evaporated ionic liquid and the parent acids and bases leads to the conclusion that vaporization as an ionic pair is preferred as larger is the difference in \(pK_a\) of the parent acids and bases. Returning to the issue of calculating thermodynamic properties of the ideal gas phase of nonprotic imidazolium ionic liquids, the agreement between calculation under the assumption of ionic pairs and experimental data gives further support for the physical picture that nonprotic ionic liquids in the gas phase are not made of isolated anions and cations.

Vibrational spectroscopy is a complementary tool for thermal analysis and mass spectrometry to reveal whether thermal decomposition of ionic liquids takes place and the nature of decomposition products. Berg et al. proposed that the Raman spectrum of 1,1,3,3-tetramethylguanidinium chloride, \([\text{TMGH}]\text{Cl}\), in the vapor phase at 225 °C was consistent with the presence of \([\text{TMGH}]\text{Cl}\) ion pairs rather than the neutral molecules 1,1,3,3-tetramethylguanidine and HCl. A Raman band at 2229 cm\(^{-1}\) was assigned to the \(N-H\) stretching mode experiencing significant lower frequency shift because of the \(N-H-Cl^{-}\) hydrogen bond. In a subsequent work, however, Berg et al. corrected this interpretation since this band was observed in exactly the same position in the Raman spectrum of vapor phase of \([\text{TMGH}]\text{Br}\). Thus, it was proposed instead that this band belongs to CN stretching mode of dimethylcyanamide, (CH\(_3\))\(_2\)N-CN, resulting from thermal decomposition of \([\text{TMGH}]\text{Cl}\) and \([\text{TMGH}]\text{Br}\). In the temperature-jump experiments of Chambreau et al., the IR spectrum is recorded for the vapor phase generated after a discharge on a filament within a small sample of the ionic liquid. For instance, characteristic IR bands of CH\(_3\)NCS indicated formation of this species upon heating of \([\text{C}_4\text{C}_1\text{im}][\text{SCN}]\), and Chambreau et al. proposed reaction mechanisms of thermal decomposition for several ionic liquids based on 1-alkyl-3-methylimidazolium cations and cyanate-ions. Liaw et al. obtained IR spectra of \([\text{C}_4\text{C}_1\text{im}][\text{C}_6\text{SO}_4]\), \([\text{C}_6\text{C}_1\text{im}][\text{Cl}]\), and \([\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]\) before and after the flash point and after ignition. Changes on the spectral pattern after ignition were considered as evidence of thermal decomposition, so that these authors claimed that flammability of these ionic liquids is related to thermal decomposition rather than vaporization of the liquid.

Vibrational assignments discussed in previous sections indicated there are some frequencies that characterize molecular conformations, whose difference of conformer energies according to quantum chemistry calculations might be relatively small in comparison with thermal energy available at room temperature. Vibrational spectroscopy has been extensively used to estimate the relative population of conformers and to obtain the thermodynamic functions characterizing conformational changes in ionic liquids. The procedure considers equilibrium between conformers, \(K = \frac{[\text{conf}2]}{[\text{conf}1]}\), and takes 153 Raman intensities, \(I_{\text{conf}1}\) and \(I_{\text{conf}2}\) (i.e., areas of appropriate Raman bands), as proportional to the concentration of conformers, \(I_{\text{conf}1} = \frac{I_{\text{conf}1}}{[\text{conf}1]}\) and \(I_{\text{conf}2} = \frac{I_{\text{conf}2}}{[\text{conf}2]}\),

\[
\ln \frac{I_{\text{conf}2}}{I_{\text{conf}1}} = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} + \ln \frac{I_{\text{conf}2}}{I_{\text{conf}1}}.
\]

Umebayashi et al. considered Raman bands of \([\text{C}_4\text{C}_1\text{im}][\text{BF}_4]\) and \([\text{C}_4\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]\) in the spectral range shown in Figure 21 and obtained \(\Delta H^o \approx 2\text{ kJ mol}^{-1}\) for the nonplanar \(\text{[C}_4\text{C}_1\text{im}]^+\) planar equilibrium of \([\text{C}_4\text{C}_1\text{im}]^+\) (i.e., the nonplanar is slightly more stable than the planar conformer). This figure of \(\Delta H^o\) obtained from Raman spectroscopy was practically the same as calculated by quantum chemistry methods for the two \([\text{C}_4\text{C}_1\text{im}]^+\) conformers. In the case of \([\text{C}_4\text{C}_1\text{im}]^+\), Holomb et al. considered the intensities of Raman bands at 808, 825, 883, and 905 cm\(^{-1}\) as characteristics of four conformers 883 gauche–gauche, gauche–anti, anti–gauche, and anti–anti, respectively, and obtained the relative populations 0.07:0.48:0.17:0.28 in the ionic liquid \([\text{C}_4\text{C}_1\text{im}][\text{BF}_4]\). Thermodynamic functions of conformational changes of \([\text{C}_4\text{C}_1\text{im}]^+\) were obtained by Umebayashi et al. from the temperature-dependence of Raman intensities of bands in the spectral range shown in Figure 20. These authors calculated \(\Delta H^o\), \(\Delta S^o\), and \(\Delta G^o\) by considering an equilibrium between only two \([\text{C}_4\text{C}_1\text{im}]^+\) conformers, anti \(\equiv\) gauche, for a sequence of ionic liquids containing chloride, bromide, and iodide. Umebayashi et al. found that both the conformers coexist in comparable quantities (i.e., \(\Delta G^o\) close to zero), even though the Raman bands of these ionic liquids indicate that the halide anion gets smaller. This spectroscopic approach for obtaining thermodynamic properties of conformational changes has been used for other cations (e.g., 1-isopropyl-3-methylimidazolium, \([\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]\), \([\text{C}_4\text{C}_1\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]\), and \([\text{C}_4\text{C}_1\text{C}_6\text{C}_1\text{im}][\text{C}_6\text{SO}_4]\)\).
Figure 12 showed Raman bands that are good markers of different conformers of \([\text{NTf}_2^-]\), so that Raman spectroscopy has been used to quantify thermodynamic properties related to conformational changes of this anion. Assuming the \([\text{NTf}_2^-]\) equilibrium as transoid \(\leftrightarrow\) cisoid, Fujii et al.\textsuperscript{124} used the 398 and 407 cm\(^{-1}\) Raman bands as markers of transoid and cisoid conformers, respectively. These authors obtained \(\Delta H^f = 3.5\) kJ mol\(^{-1}\) from the Raman spectra of \([\text{C}_2\text{C}_1\text{im}][\text{NTf}_2^-]\) in close agreement with ab initio calculations of the isolated anion, 2.2–2.5 kJ mol\(^{-1}\), depending on the level of theory. Lassègues et al.\textsuperscript{111} considered the spectral range of 260–360 cm\(^{-1}\) shown in Figure 12 and found that the relative population of transoid \([\text{NTf}_2^-]\) conformer is 75% in \([\text{C}_2\text{C}_1\text{im}][\text{NTf}_2^-]\) at room temperature but a slightly higher value for the enthalpy, \(\Delta H^f = 4.5\) kJ mol\(^{-1}\). Essentially the same \(\Delta H^f\) for conformational change of \([\text{NTf}_2^-]\) was obtained in N-alkyl-N-methylpyrrolidinium ionic liquids.\textsuperscript{126,127} A distinctive feature of a Raman spectroscopic study performed by Martellini et al.\textsuperscript{116} for some nonprotic and protic ionic liquids was that \(\Delta H^f\) of \([\text{NTf}_2^-]\) conformational change was also obtained from the intense Raman band at 740 cm\(^{-1}\). This band exhibits a slightly asymmetric shape toward the low-wavenumber side, so that two components at 738 and 741 cm\(^{-1}\) resulting from the curve fit have been assigned to cisoid and transoid \([\text{NTf}_2^-]\) conformers, respectively. The analysis of the temperature dependence of the band shape gave \(\Delta H^f\) in reasonable agreement with the value obtained from the analysis of the 260–360 cm\(^{-1}\) spectral range.\textsuperscript{116} Plots \(\ln(\text{I}_{\text{trans}}/\text{I}_{\text{cis}})\) versus \(T^{-1}\) for bands that characterize transoid and cisoid \([\text{NTf}_2^-]\) conformers also offer spectroscopic signatures of the glass transition of glass-forming ionic liquids. Palumbo et al.\textsuperscript{259} considered IR bands in the range of 500–650 cm\(^{-1}\) to characterize \([\text{NTf}_2^-]\) conformers in an ammonium-based ionic liquid: the linear Arrhenius plot above the glass transition temperature (\(T_g \sim 210\) K) changes slope at \(T_g\) and becomes constant indicating that the relative concentration of \([\text{NTf}_2^-]\) conformers does not change any longer in the glassy phase.

Moschovi et al.\textsuperscript{118} paid attention to appropriate corrections on the raw spectral data prior the analysis of equilibrium by Raman spectroscopy. As already warned by Papatheodorou et al.\textsuperscript{2} in their review on molten salts, these corrections include accounting for polarization by using the isotropic component of the Raman spectrum, the excitation wavelength dependence, and the Boltzmann population factor. In the liquid phase of protic \([\text{C}_2\text{im}][\text{NTf}_2^-]\), which melts at \(T_m \sim 325\) K, Moschovi et al.\textsuperscript{118} found significantly higher enthalpy for conformational change of \([\text{NTf}_2^-]\) when these corrections are taken into account, 8.5 kJ mol\(^{-1}\), in comparison with the analysis performed using raw spectra (6.0 kJ mol\(^{-1}\)). Taking a sequence of protic ionic liquids \([\text{C}_2\text{im}][\text{NTf}_2^-]\) with increasing length of the alkyl chain \((n = 4, 6, 8, 10, 12, 14, 16, \ldots)\), Moschovi et al.\textsuperscript{199} claimed that the population of \([\text{NTf}_2^-]\) conformers and the corresponding \(\Delta H^f\) are signatures of the relative importance of anion–cation interaction by Coulombic forces in comparison with other contributions to intermolecular forces (hydrogen bond, van der Waals, and dispersion due to \(\pi-\pi\) interaction). These authors proposed that as the alkyl chain of \([\text{C}_n\text{im}][\text{NTf}_2^-]\) increases, leading to segregation of nonpolar and polar domains, then \([\text{NTf}_2^-]\) experiences a local environment in which the transoid conformation is favored. The population of cisoid conformer increases with temperature proper to the positive \(\Delta H^f\) value, which however becomes less positive the longer the \([\text{C}_n\text{im}][\text{NTf}_2^-]\) alkyl chain.\textsuperscript{199} On the other hand, the way that the transoid over cisoid ratio \(I_{\text{trans}}/I_{\text{cis}}\) increases with the chain length is different for protic and nonprotic ionic liquids: \(I_{\text{trans}}/I_{\text{cis}}\) reaches a plateau when \(n = 4\) in \([\text{C}_4\text{im}][\text{NTf}_2^-]\) whereas it gradually increases up to \(n = 12\) in \([\text{C}_4\text{im}][\text{NTf}_2^-]\).\textsuperscript{201}

In the case of \([\text{N}(\text{SO}_2\text{F})_2]^+\), Fujii et al.\textsuperscript{129} obtained essentially the same enthalpy of conformational change as \([\text{NTf}_2^-]\) from the analysis of the temperature dependence of the Raman bands of \([\text{C}_2\text{C}_1\text{im}][\text{N}(\text{SO}_2\text{F})_2]\) within 280–380 cm\(^{-1}\) (see this spectral range in Figure 14). If the \([\text{N}(\text{SO}_2\text{F})_2]^+\) anion is in the ionic liquid based on the N-methyl-N-propylpyrrolidinium cation, the \(\Delta H^f\) of the \([\text{N}(\text{SO}_2\text{F})_2]^+\) conformational change is slightly higher, 6.8 kJ mol\(^{-1}\).\textsuperscript{275}

Investigating molecular conformations in condensed phase is a common issue for molecular dynamics (MD) simulations of ionic liquids. Classical MD simulation relies on an assumed potential energy function including intermolecular interactions, which are normally described by Lennard-Jones potential and Coulombic interactions between partial atomic charges and an intramolecular force field accounting for molecular vibrations.\textsuperscript{260} The validation of a proposed model is accomplished by comparing thermodynamic, structural, and dynamical properties calculated by MD simulations and experimental data.\textsuperscript{261} Nevertheless, vibrational spectra are the source of data for reasonable parameters of force constants needed for the intramolecular terms of the potential function. The well-known force field of Canongia Lopes and Pádua (CL&P)\textsuperscript{75} has been tested taking into account information on conformers distribution available from vibrational spectroscopy. Focusing here on the intramolecular part of the CL&P model, \(V_{\text{int}}\) this includes bond stretching, \(r\), angle bending, \(\theta\), and torsion of dihedral angles, \(\psi\):

\[
V_{\text{int}} = \sum_{\text{bonds}} \frac{k}{2} (r - r_{eq})^2 + \sum_{\text{angles}} \frac{k}{2} (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \frac{\sum_{m=1}^{4} k_{\psi,m} [1 + (-1)^m \cos(m\psi) - 1]}{2}
\]

where \(r\) and \(\theta\) are equilibrium bond length and angle. Force constants of stretching and bending, \(k\), and \(k_{\psi}\) used in MD simulations of ionic liquids are usually taken from previous force fields (e.g., AMBER and OPLS-AA). It is worth noting that due to the harmonic oscillator model for stretching and bending modes, the condensed phase effect on vibrational frequency shift is not the issue being addressed by this kind of model. In fact, proper coupling between intra- and intermolecular degrees of freedom is very dependent on anharmonicity of the probe oscillator.\textsuperscript{80,79} On the other hand, special attention was given in the CL&P model for \(k_{\psi}\) parameters. The dihedral angle terms should give potential energy profiles of torsion consistent with quantum chemistry calculations and the distribution of conformers resulting from 209 analyses of Raman spectra. For instance, in the case of 1-alkyl-3-methylimidazolium cations,\textsuperscript{296} the relative population of gauche and anti conformers calculated by MD simulations was compared with the analysis of the 600–700 cm\(^{-1}\) spectral range, which includes the Raman bands that characterize cation conformers.

Understanding macroscopic properties of ionic liquids on the basis of intermolecular interactions is a major aim that vibrational spectroscopy shares with other experimental techniques and theoretical methods. IR spectroscopy provides one of the most characteristic experimental evidence of the X−...
H–Y hydrogen bond: the vibrational frequency of the X–H stretching mode shifts to lower wavenumber (red shift) in comparison with the isolated X–H oscillator.\textsuperscript{263–267} Other spectroscopic features usually accompanying the $\nu(X-H)$ red shift on hydrogen bond formation include the enhancement of IR intensity and broadening of this band and the increase of vibrational frequency (blue-shift) of the bending mode $\delta$(X–H). Applying vibrational spectroscopy for studying pure ionic liquids aims insights on the strength and atomic sites involved in hydrogen bonds and, within a more general viewpoint, on the overall nature of anion–cation interactions. Katsyuba et al.\textsuperscript{48} provided a detailed comparison between experimental frequencies and ab initio calculations for different ion pair configurations of 1-alkyl-3-methylimidazolium cations and [BF$_4$]$^-$ or [PF$_6$]$^-$. Frequencies related to C–H stretching and out-of-plane vibrations of the imidazolium ring and $\nu(B-F)$ ofr(P–F) are sensitive to ion pair formation. Katsyuba et al.\textsuperscript{46} advocate that IR bands belonging to $\nu(C_1(3)-H)$ and $\nu(C_2(5)-H)$ modes ($\sim3100$ cm$^{-1}$) are separated from the red-shifted $\nu(C_2(2)-H)$ mode ($\sim3120$ cm$^{-1}$) because the C$_{3}$H$_{2}$···F interaction is stronger than C$_{4}$(5)···H···F interactions.

This assignment of C–H stretching modes\textsuperscript{54,119,53,175,177,48} and the alternative interpretation that the doublet of bands in the high-frequency range of 1-alkyl-3-methylimidazolium vibrations is due to Fermi resonance,\textsuperscript{52,168,169} have already been addressed in section 4.2.1. In a subsequent work, Katsyuba et al.\textsuperscript{208} preferred to call these bands as($C_{\text{aromatic}}-H$) being aware of the role played by Fermi resonance in the spectral range of C–H stretching modes. These authors investigated imidazolium ionic liquids with a terminal -OH group in the side chain [HO-C$_2$C$_1$im]$^+$ (see Figure 25) and different fluorinated anions. Vibrational frequencies of both $\nu(C_{\text{aromatic}}-H)$ and $\nu(O-H)$ decrease, and the bands become broader, as the anion basicity increases.\textsuperscript{208}

It is worth noting that the intensity of the lower frequency $\nu(C_{\text{aromatic}}-H)$ component ($3100–3130$ cm$^{-1}$) increases in relation to the higher frequency component of the doublet ($3150–3170$ cm$^{-1}$) with increasing strength of anion–cation hydrogen bond.\textsuperscript{208} Taking for granted the assignment of these bands alk(C$_3$-H) and $\nu(C_4(3,5)-H)$, respectively, these findings have been considered signatures of stronger H-bonding through the more acid C$_2$-H site of dialkyl-substituted imidazolium cations. Some empirical relationships between vibrational frequency shift, $\Delta\nu = \nu(XH^\text{free}) - \nu(XH^\text{bonded})$, and the enthalpy of hydrogen bond formation, $-\Delta H_{\text{H}}$, are well-known.\textsuperscript{265,266} Katsyuba et al.\textsuperscript{208} estimated $-\Delta H_{\text{H}}$ for hydrogen bonding between [HO-C$_2$C$_1$im]$^+$ and fluorinated anions from both $\nu(C_{\text{aromatic}}-H)$ and $\nu(O-H)$ modes, covering a rather large range depending on the anion basicity, $1.6-10.0$ kJ mol$^{-1}$.\textsuperscript{2370}

In contrast, Moschovi et al.\textsuperscript{199} kept the same [NTf$_2$]$^-$ anion, while investigating how the hydrogen bond strength depends on the alkyl chain length of protic imidazolium cations, [C$_n$im]$.^+$ They found that vibrational frequencies of both $\nu(C_{\text{aromatic}}-H)$ and $\nu(N-H)$ modes of [C$_n$im]$^+$ are red-shifted as $n$ increases.\textsuperscript{199} Garaga et al.\textsuperscript{200} obtained the same results for $\nu(C_{\text{aromatic}}-H)$ modes in nonprotic [C$_3$C$_{1}$im][NTf$_2$] ionic liquids. However, these findings were assigned to the intramolecular inductive effect of longer alkyl chain rather than an effect on the strength of the anion–cation hydrogen bond.\textsuperscript{2380}

The works of Katsyuba et al.\textsuperscript{48,208} and Moschovi et al.\textsuperscript{199,201} mentioned above illustrate the application of IR and Raman spectroscopies to infer about structural features both in nonpolar and polar domains of ionic liquids. In fact, the combined usage of vibrational spectroscopy and quantum chemistry calculations covers a large literature of ionic liquids,\textsuperscript{2386} part of it already considered in the previous sections. On the other hand, in an attempt to correlate with melting temperature, Katsyuba et al.\textsuperscript{48} put forward the proposition that it is the anharmonicity of the intermolecular anion–cation vibration, rather than the interaction energy of an ionic pair, that determines the melting temperature of ionic liquids. Their conclusion was based on quantum chemistry calculation of the potential energy curve as a function of anion–cation distance. Direct evidence of the intermolecular anion–cation vibration is the realm of far-IR and low-frequency Raman spectroscopies to be discussed in the next section.

Some works went further on quantum chemistry calculations\textsuperscript{2399} of vibrational spectra by considering clusters of ions instead of a single ionic pair. Dong et al.\textsuperscript{269} calculated the IR spectrum of 1[C$_2$C$_{1}$im][BF$_4$] at the DFT/B3LYP level of theory for clusters of ions ([C$_2$C$_{1}$im][BF$_4$])$_n$ with increasing size, $n = 2, 3, 4$, and 5. The overall appearance of theoretical IR spectrum (peak positions, band shapes, and relative intensities, including the FIR range) gets closer to the experimental spectrum of liquid 1[C$_2$C$_{1}$im][BF$_4$] with increasing cluster size.\textsuperscript{269} Thus, there is an incipient hydrogen bond network making the five ion pairs cluster a microscopic model of bulk [C$_2$C$_{1}$im][BF$_4$]. The need for considering ion clusters in order to the full appearance of vibrational spectra being recovered by ab initio calculations is particularly demanding for protic ionic liquids. Bodo et al.\textsuperscript{242} calculated the Raman spectrum of methylammonium nitrate by considering clusters whose structures were first generated by classical MD simulations and then optimized at the DFT/B3LYP level of theory. It is worth remembering that such calculations of clusters still concern harmonic vibrational frequencies, so that scaling factors are needed for better agreement between calculation and experiment. Nevertheless, the Raman spectra calculated for clusters ([C$_2$NH$_3$][NO$_3$])$_n$ at $n = 2, 4, 6$, and 8, exhibit distribution of frequencies that become broader as the cluster size increases.\textsuperscript{240} In a subsequent work, Bodo et al.\textsuperscript{241} extended the calculations of Raman spectra for the series ethyl-, propyl-, and butylammonium nitrate. Thus, the ab initio calculation of reasonable structures of clusters of ions captures some key features of ionic interactions that are important for the calculation of vibrational frequencies, in particular the strength distribution of anion–cation hydrogen bonds.\textsuperscript{2429}

The nitrate anion can be used as an example of taking an anion vibration, $\nu$(NO$_3$), rather than C–H, N–H, or O–H stretching modes, as a probe of the difference in width in the distribution of hydrogen bond strengths between protic and nonprotic ionic liquids. Figure 34 shows the $\nu$(NO$_3$) Raman band in [C$_2$C$_{1}$im][NO$_3$] and [C$_3$NH$_3$][NO$_3$]. Stronger anion–cation interaction in [C$_3$NH$_3$][NO$_3$] in comparison with [C$_2$C$_{1}$im][NO$_3$] implies +3.5 cm$^{-1}$ shift of $\nu$(NO$_3$) and a remarkable broadening and asymmetry of the band because of the distorted hydrogen bond network in the protic liquid.\textsuperscript{2439} Full width at half height (fwhh) of the $\nu$(NO$_3$) Raman band in [C$_2$C$_{1}$im][NO$_3$] and [C$_3$NH$_3$][NO$_3$] is 5.0 and 11.0 cm$^{-1}$, respectively. For comparison purposes, fwhh is $\sim$15.0 cm$^{-1}$ in 442 molten NaNO$_3$ at 600 K and $\sim$6.0 cm$^{-1}$ in [NO$_3$]$^-$ aqueous solution at room temperature.\textsuperscript{2470} DFT calculation performed by Faria et al.\textsuperscript{245} showed that $\nu$(NO$_3$) vibrational frequencies 2445

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of anions in a cluster ([C₂NH₃][NO₃])₄ indeed cover the spectral range of bandwidth of the experimental spectrum. Ionic liquids whose vibrational spectra have been interpreted with the help of ab initio MD simulations include those based on 1-alkyl-3-methylimidazolium with cyanoanions or acetate, alkylammonium with nitrate or bromide and choline with carboxylates or amino acid anions. Ab initio MD simulations of ionic liquids go further than calculations of minimum energy structures by taking into account the liquid phase dynamics and anharmonicity of vibrations. Wendler et al. found that the calculation of phase liquid IR spectra of imidazolium ionic liquids exhibit a spectral pattern significantly different from the single ion pair calculation. The calculation of ion pair strongly favors the anion pointing toward the C(2)−H bond of the imidazolium ring, whereas ab initio MD simulation explores a distribution of anions around cations. Extreme examples of this situation is [C₂C₇im][CH₃COO], for which quantum chemistry calculation of a single pair leads to the formation of hydrogen-bonded carbene−acetic acid with an IR band at 2167 cm⁻¹, which is however not seen in the experimental spectrum nor in the spectrum calculated by ab initio MD simulation of the liquid phase. Wendler et al. found that including eight ionic pairs in the calculations was enough to capture the most important dynamics on the point of view of vibrational spectroscopy (i.e., the short-time dynamics of ions rattling inside the cages made by the neighbors).

Bodo et al. calculated the vibrational frequencies of [C₂NH₃][NO₃] by ab initio MD simulation of clusters of 6 or 24 ionic pairs. The experimental Raman spectrum of [C₂NH₃][NO₃] was compared to the power spectrum obtained by Fourier transforming the autocorrelation function of atomic vibrations with very different Raman activities, so that they calculated a distribution of anions around cations. Extreme examples of this situation is [C₂C₇im][CH₃COO], for which quantum chemistry calculation of a single pair leads to the formation of hydrogen-bonded carbene−acetic acid with an IR band at 2167 cm⁻¹, which is however not seen in the experimental spectrum nor in the spectrum calculated by ab initio MD simulation of the liquid phase. Wendler et al. found that including eight ionic pairs in the calculations was enough to capture the most important dynamics on the point of view of vibrational spectroscopy (i.e., the short-time dynamics of ions rattling inside the cages made by the neighbors).

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anion proposed that methylation of the C(2) site of the imidazolium ring results in more viscous ionic liquid. It has also been methylation of the most acidic hydrogen of the imidazolium bonds act like defects perturbing the charge symmetry of the site available for stronger hydrogen bond because hydrogen
[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[NTf}_2\text{]}$, even though the former has the C(2) site available for stronger hydrogen bond because hydrogen
\[\text{C}_2\text{C}_1\text{C}_1\text{im}\] even though the former has the C(2) site available for stronger hydrogen bond because hydrogen
\[\text{C}_2\text{C}_1\text{C}_1\text{im}\] even though the former has the C(2) site available for stronger hydrogen bond because hydrogen

Figure 35. FIR spectra of some aprotic ionic liquids based on imidazolium cations with $[\text{BF}_4]$ or $[\text{NO}_3]$ and the protic ionic liquid propylanmonium nitrate. The arrow on the top of the low-frequency feature indicates the band assigned to the stretching mode of anion–cation hydrogen-bonded. Bands in the gray area belong to intra-molecular normal modes. Reproduced with permission from ref 274. Copyright 2009 PCPCC Owner Societies.

spectra as the density of states by analogy to low-frequency spectra of glass forming liquids (see eq 10 below). Schwenzer et al.\textsuperscript{144} assigned anion–cation hydrogen bond vibrations in FIR spectra of $[\text{C}_n\text{C}_1\text{im}]\text{[CF}_3\text{SO}_3\text{]}$ and $[\text{C}_n\text{C}_1\text{im}]\text{[HSO}_4\text{]}$ to bands observed at 80 and 103 cm$^{-1}$, respectively. A distinctive feature in the FIR spectrum of $[\text{C}_4\text{C}_1\text{im}]\text{[HSO}_4\text{]}$ are additional bands that Schwenzer et al.\textsuperscript{144} with the support of MD simulations and NMR spectroscopy, assigned to hydrogen-bonded $[\text{HSO}_4]^-$ anions. The occurrence of anion–anion hydrogen bonding in $[\text{HSO}_4]^-$ ionic liquids is in line with the proposition of Ribeiro\textsuperscript{156} based on the analysis of high-frequency Raman bands of $[\text{HSO}_4]^-$.

Fumino et al.\textsuperscript{276,277} argued that strong hydrogen bonds in the protic ionic liquids ammonium nitrate imply higher frequencies for anion–cation intermolecular vibrations. The similarity between FIR spectra of ammonium nitrate and water led Fumino et al.\textsuperscript{276} to the proposition of a three-dimensional hydrogen bond network in these protic ionic liquids. In the case of imidazolium ionic liquids, Fumino et al.\textsuperscript{286} found that the maximum of the FIR band for $[\text{C}_n\text{C}_1\text{im}]\text{[X]}$, $n = 3, 4, 5$, and 6, does not depend on the alkyl chain length and follows the trend 72.5, 92, and 122 cm$^{-1}$ for the halide anions $\Gamma^-$, $\text{Br}^-$, and $\text{Cl}^-$, respectively. Yamada et al.\textsuperscript{278} argued that these frequencies are on the same proportion of the inverse of the square root of reduced mass for the vibration of anion and imidazolium ring. However, Fumino et al.\textsuperscript{274,279,281} compared the position of the FIR band for a large set of ionic liquids and showed that only the mass effect does not account for the 292 vibrational frequency shift. These authors performed quantum chemistry calculations for clusters of ionic pairs and correlated FIR frequencies with binding energies, thus supporting the interpretation of frequency shifts as the result of different anion–cation force constants.\textsuperscript{273,274,277,281,283,284,286 Further-} more, Fumino et al.\textsuperscript{282} showed that the vibrational frequency of 298 the main spectral feature in the FIR spectrum correlates with the enthalpy of vaporization of the ionic liquid.

A step forward along the combined usage of FIR spectroscopy and DFT calculations was the attempt at separating the relative contributions of hydrogen bonding and dispersion forces out of the total energy, which is predominantly Coulombic energy.\textsuperscript{284–286} Fumino et al.\textsuperscript{284,286} measured FIR spectra as a function of temperature (303–353 K) for protic ammonium ionic liquids with appropriately chosen alkyl chain length and anions in order to play with the relative strengths of hydrogen bonding and dispersion forces. Bands assigned to $\delta(C\cdotsH\cdotsA)$ and $\nu(C\cdotsH\cdotsA)$ were seen in the FIR spectrum of $[\text{C}_4\text{C}_1\text{C}_1\text{NH}][\text{CF}_3\text{SO}_3]$ as two resolved peaks around 70 and 130 cm$^{-1}$, respectively, as temperature decreases. When 292 temperature increases, the FIR spectrum is dominated by a single broad band with maximum at 100 cm$^{-1}$, which has been assigned to the anion interacting with the cation alkyl chains (i.e., an ion pair determined by dispersion forces). The temperature dependence of relative intensities of FIR bands assigned to local arrangements dominated by hydrogen bonds and dispersion forces allowed for a van’t Hoff analysis of the equilibrium between these two kinds of ion pairs.\textsuperscript{284} The van’t Hoff plot indicated that the hydrogen-bonded ion pair is 292 favored by ~34 kJ mol$^{-1}$ over the dispersion-interaction dominated structure. This experimental finding pointed out the need for proper consideration of dispersion corrected methods in DFT calculations of ion pair energies.\textsuperscript{284–286,282}

Fumino et al.\textsuperscript{193} and Buffeteau et al.\textsuperscript{287} addressed the effect of methylation of the C(2)–H position of the imidazolium ring by 297 comparing the FIR spectra of $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[NTf}_2\text{]}$ and $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[BrF}_3\text{]}$. FIR bands of $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[NTf}_2\text{]}$ and $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[BF}_3\text{]}$ were found respectively at 83.5 and 79.9 cm$^{-1}$ by Fumino et al.\textsuperscript{193} and 82.5 and 73 cm$^{-1}$ by Buffeteau et al.\textsuperscript{283}. Analogous effect of methylation of the imidazolium ring is seen in the FIR spectra of $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[BF}_3\text{]}$ and $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[BTf}_2\text{]}$ shown in Figure 35. In addition to the red shift of 294 vibrational frequency, Fumino et al.\textsuperscript{193} found that the intensity of the FIR band decreases because of weakening of the anion–cation hydrogen bonding as the stronger binding site C(2)–H is switched off in $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[NTf}_2\text{]}$. In contrast, Buffeteau et al.\textsuperscript{283} have not found significant difference in the FIR intensity between $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[NTf}_2\text{]}$ and $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[BF}_3\text{]}$ after proper normalization by the intensities of high-frequency intra-molecular bands. Buffeteau et al.\textsuperscript{287} also compared FIR spectra of $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[NTf}_2\text{]}$ and $[\text{C}_2\text{C}_1\text{C}_1\text{im}]\text{[BF}_3\text{]}$ and they found 294 essentially the same intensity and vibrational frequency for both the systems. Therefore, Buffeteau et al.\textsuperscript{287} reached the opposite conclusion.
Conclusion, claiming that the characteristic broad band in FIR spectra should not be assigned exclusively to stretching mode of the anion—cation bond. These authors preferred instead assigning the density of states revealed by the FIR spectrum as a kind of envelope over the solidlike lattice vibrations. This physical picture is akin the one resulting from low-frequency Raman spectroscopy studies of phase transitions of ionic liquids to be discussed in the next section.

Wulf et al.\textsuperscript{288} compared FIR to low-frequency Raman spectra, and also Terahertz (THz) spectra, for the same set of ionic liquids ([C\textsubscript{4}C\textsubscript{1}im][SCN], [C\textsubscript{4}C\textsubscript{1}im][N(CN)\textsubscript{2}], [C\textsubscript{4}C\textsubscript{1}im][C\textsubscript{2}SO\textsubscript{4}], and [C\textsubscript{4}C\textsubscript{1}im][NTf\textsubscript{2}]) previously studied by Fumino et al.\textsuperscript{273} It has been found that the spectral pattern and optical constants obtained from FIR spectra of imidazolium ionic liquids agree with data obtained by THz spectroscopy.\textsuperscript{278,279,287,288} However, the experimental setup of Wulf et al.\textsuperscript{288} did not allow obtaining reliable Raman spectra below 100 cm\textsuperscript{-1} so that the comparison between FIR and low-frequency Raman was restricted to intramolecular bending modes of cations or anions observed in the range of 150–300 cm\textsuperscript{-1}.

Low-frequency Raman spectroscopy investigations of inter- molecular dynamics encompass a large literature with a special focus on glass-forming liquids\textsuperscript{289–291} and among them several high (temperature) molten salts (e.g., alkali halides,\textsuperscript{294–296} ZnCl\textsubscript{2},\textsuperscript{297,298} BiCl\textsubscript{3},\textsuperscript{298,299} mixtures ZnCl\textsubscript{2}–AlCl\textsubscript{3},\textsuperscript{300} etc.).\textsuperscript{1,2} An early study of the low-frequency range was reported by Ribeiro et al.\textsuperscript{281} for the low-temperature molten salt tetra(n-buty)-ammonium croconate, [C\textsubscript{4}C\textsubscript{4}C\textsubscript{1}im][C\textsubscript{4}O\textsubscript{4}]·4H\textsubscript{2}O, which is a glass-forming liquid with\textit{T}_g = 293 K. The first low-frequency Raman spectroscopy studies concerning nowadays typical ionic liquids were reported by Ribeiro\textsuperscript{282} for [C\textsubscript{4}C\textsubscript{1}im][PF\textsubscript{6}], as a function of temperature and by Iwata et al.\textsuperscript{283} for [C\textsubscript{6}C\textsubscript{1}im][BF\textsubscript{4}], [C\textsubscript{4}C\textsubscript{1}im][PF\textsubscript{6}], [C\textsubscript{6}C\textsubscript{1}im][PF\textsubscript{6}], and [C\textsubscript{8}C\textsubscript{1}im][PF\textsubscript{6}] at room temperature.

In these works, the low-frequency Raman spectrum is conveniently reported after discounting a thermal population factor from the raw experimental spectrum, $I(\omega)$, in the so-called susceptibility representation, $\chi(\omega)$:

$$\chi(\omega) = -\frac{I(\omega)}{n(\omega) + 1}$$

(8)

where

$$n(\omega) = \frac{1}{e^{\hbar \omega/kT} - 1}$$

(9)

The motivation behind the reduction of the low-frequency Raman spectrum is the relation between $I(\omega)$ and the density of vibrational states $g(\omega)$:\textsuperscript{303,304}

$$I(\omega) = \frac{n(\omega) + 1}{\omega} C(\omega) g(\omega)$$

(10)

where $C(\omega)$ is the light-vibration coupling. The spectral pattern of $g(\omega)$ corresponds to the power spectrum alluded for in section 3, and $C(\omega)$ accounts for how the low-frequency vibrations modulate the material polarizability.

Figure 36 shows the raw low-frequency Raman spectrum of [C\textsubscript{4}C\textsubscript{1}im][NTf\textsubscript{2}] at room temperature, and the resulting $\chi(\omega)$ (inset in the top panel). The relatively sharp bands above 100 cm\textsuperscript{-1} belongs to intramolecular modes of the [NTf\textsubscript{2}]\textsuperscript{–} anion (see Figure 11 and Table 2). If the frequency-dependence of $C(\omega)$ were linear then $\chi(\omega)$ would give directly the density of vibrational states. The actual frequency dependence of $C(\omega)$ is experimentally accessible by comparing the Raman spectrum with $g(\omega)$ obtained by neutron scattering spectroscopy.\textsuperscript{298,305} Another common representation of the low-frequency spectrum is the reduced Raman intensity, $I_{\text{red}}(\omega) = \chi(\omega)/\omega$.\textsuperscript{274} Since the factor $n(\omega) + 1$ depends linearly with $\omega$ at low-frequency, $I_{\text{red}}(\omega)$ is similar to the experimental $I(\omega)$, whereas the low-frequency bands are slightly shifted to higher frequencies in the $\chi(\omega)$ representation.\textsuperscript{306} In order to highlight that the low-frequency bands are not artifact of the $\chi(\omega)$ representation, the bottom panel of Figure 36 shows the raw Raman spectra, $I(\omega)$, of [C\textsubscript{4}C\textsubscript{1}im][NTf\textsubscript{2}] as a function of temperature. Low-frequency Raman band assigned to intermolecular vibration is clearly seen in the raw spectrum of [C\textsubscript{4}C\textsubscript{1}im][NTf\textsubscript{2}] as the glass transition temperature, $T_g = 181$ K, is achieved from above. The quasi-elastic component is due to anharmonicity and fast relaxation processes, so that its intensity decreases significantly with decreasing temperature.\textsuperscript{295–297,299,300,307–310} In fact, the plot of the quasi-elastic intensity versus temperature exhibits break of slope at the glass-transition temperature for several ionic liquids.\textsuperscript{302,311,312}

The optical Kerr effect (OKE) spectrum is equivalent to the depolarized Raman spectrum, the results of these techniques differing by the population factor.\textsuperscript{113} It has been found that the depolarization ratio is essentially constant at 0.75 in the low-frequency range of the Raman spectrum of [C\textsubscript{4}C\textsubscript{1}im][PF\textsubscript{6}].\textsuperscript{302} In other words, essentially the same band shape is obtained in the low-frequency range for polarized, depolarized, or without polarization selection of the scattered radiation. It is worth noting that the frequency-dependent depolarization ratio has been found in Raman spectra of high temperature molten salts, especially when complex molecular-like structures occur in the melt.\textsuperscript{289,299,314} In the case of ionic liquids, the intermolecular vibrational dynamics has been much more investigated by OKE\textsuperscript{315–320} than low-frequency Raman spectroscopy. Both OKE and Raman spectroscopies probe polarizability fluctuations.
B.C.

The anion–cation hydrogen bond vibrations are not expected to give as intense signals in Raman as in FIR spectra. The distinctive features of low-frequency Raman spectra are made clearer in the right panel of Figure 37 showing the spectra for \([\text{C}_4\text{C}_1\text{im}] \text{[BF}_4]\) and \([\text{C}_3\text{NH}_3] \text{[NO}_3]\), which are two systems corresponding to the extreme cases of FIR spectra shown in Figure 35. The significant frequency shift in the FIR spectrum when moving from the nonproton \([\text{C}_4\text{C}_1\text{im}] \text{[BF}_4]\) to the proton \([\text{C}_3\text{NH}_3] \text{[NO}_3]\) (see Figure 35) is not manifest in the low-frequency Raman spectra. The \(\chi'(\omega)\) spectra of \([\text{C}_4\text{C}_1\text{im}] \text{[NTf}_2]\) and \([\text{C}_4\text{C}_1\text{im}] \text{[BF}_4]\) (black lines in the right and left panels of Figure 37) are similar, except for the \([\text{NTf}_2]^−\) normal mode at 120 cm\(^{-1}\), which is evidently absent in the spectrum of the latter. On the other hand, the spectral patterns of \(\chi'(\omega)\) for the two ammonium ionic liquids shown by red and pink lines in the right and left panels of Figure 37 differ in relative intensities of the components encompassing the band shape.

The intense component with maximum at \(\sim 70\) cm\(^{-1}\) in the \(\chi'(\omega)\) spectrum of \([\text{C}_4\text{C}_1\text{im}] \text{[NO}_3]\) has also been found by Sonnleitner et al.\(^{23}\) in OKE spectra of ethyl- and propylammonium nitrate. This spectral feature is close to the FIR band at \(\sim 60\) cm\(^{-1}\), which Fumino et al.\(^{26}\) assigned to the binding of the anion–cation hydrogen bond. Krüger et al.\(^{24}\) followed the Fumino et al.\(^{26}\) assignment for the corresponding feature observed at \(\sim 40\) cm\(^{-1}\) in the THz spectrum of ethylammonium nitrate. However, Sonnleitner et al.\(^{23}\) assigned the band at \(\sim 70\) cm\(^{-1}\) to \([\text{NO}_3]^-\) libration (i.e., restricted out-of-plane rotation about the \(\text{C}_2\) axes of \([\text{NO}_3]^-\)) because OKE spectroscopy is primarily sensitive to rotational motions and to the large polarizability anisotropy of the \([\text{NO}_3]^-\) anion. It is worth mentioning that the additional band assigned to libration of aromatic ring is also found at 60 cm\(^{-1}\) in the OKE spectrum when a phenyl group is attached to the longer chain of the 18-membered imidazolium cation.\(^{32}\) The long tail extending up to 250 cm\(^{-1}\) in the \(\chi'(\omega)\) spectrum of \([\text{C}_3\text{NH}_3] \text{[NO}_3]\) is absent in the \([\text{C}_4\text{C}_1\text{C}_3\text{C}_1\text{N}] \text{[NTf}_2]\) spectrum (compare red lines in right and left panels of Figure 37). On the basis of curve fitting, Sonnleitner et al.\(^{23}\) proposed that the high-frequency tail in the OKE spectra of \([\text{C}_3\text{NH}_3] \text{[NO}_3]\) and \([\text{C}_3\text{NH}_3] \text{[NO}_3]\) includes unresolved bands due to hydrogen bond stretching and cation librational motions. It is worth mentioning, however, early Raman spectroscopic studies on molten alkali nitrates in which broad bands assigned to \([\text{NO}_3]^-\) libration have been found at \(\sim 26\) cm\(^{-1}\) in molten KNO\(_3\), NaNO\(_3\), and LiNO\(_3\), respectively.\(^{32}\) Thus, the high-frequency tail in the \(\chi'(\omega)\) spectrum of \([\text{C}_3\text{NH}_3] \text{[NO}_3]\) might also manifest an inhomogeneous width.
distribution of librations in this protic ionic liquid, being the low-frequency counterpart of the previous discussion (see Figure 34) concerning the Raman band shape of $\nu_1$(NO$_2$).

Despite similarities in positions of the components after curve fit of these featureless bands, low-frequency Raman and IR active intermolecular modes are not necessarily the same. Within the context of large literature about intermolecular vibrational dynamics of glass-forming liquids, the band at $\sim$20 cm$^{-1}$ seen in low-frequency Raman spectra of the glassy phase of ionic liquids (see Figure 36) is the so-called boson peak.

It has been pointed out that the boson peak vibrations remain in the liquid state even though the peak is hidden under the intense quasi-elastic scattering of the low-frequency Raman spectrum. In an OKE spectroscopy study of 1-ethyl-3-methylimidazolium tosylate, Li et al. assigned to the boson peak dynamics the oscillatory component with period of $\sim$2.0 ps (i.e., $\sim$17 cm$^{-1}$) seen in the time domain data a few degrees above the glass transition temperature ($T_g$ = 201 K). The partial nature of longitudinal and transverse acoustic modes of the intermolecular dynamics in the spatial range of wavevectors $0.1 < k < 1.0$ Å$^{-1}$ and frequency range $0 < \omega < 100$ cm$^{-1}$ in viscous glass-forming liquids has been established in many studies by inelastic X-ray scattering spectroscopy and MD simulations. Although the exact origin of the boson peak is yet a lively debated issue, several studies have been pointing to the nature of transverse acoustic vibrations of high wave-vectors (i.e., soundlike modes of short wavelength). It is worth stressing that projecting into soundlike modes recovers only the other part is random phase motion and eventually molecular-like normal modes in high temperature molten salts in which complexes survive for a relatively long time.

The assignment of FIR spectra by Fumino et al. focused on local motions related to stretching and bending modes of ion pairs, whereas assignment of low-frequency Raman and OKE spectra emphasized librational and cage-rattling motions or the many body nature of the intermolecular dynamics. Shirota considered the average frequency ($\nu$), the first moment $M_1 = \int\omega I(\omega)d\omega/\int I(\omega)d\omega$ as a single quantitative parameter for the whole low-frequency range of the OKE spectrum. It has been found that $M_1$ obtained from OKE spectrum of nonaromatic ionic liquids correlates with ($\gamma/\rho$)$^{1/2}$, where $\gamma$ is the surface tension and $\rho$ is the density. The correlation between $M_1$ and ($\gamma/\rho$)$^{1/2}$ is analogous to a simple harmonic oscillator result for the dependence of vibrational frequency with force constant and reduced mass ($k/\mu$)$^{1/2}$, however, involving the surface tension as a bulk property related to the strength of intermolecular forces.

Comparison between Figures 35 and 37 indicates that the overall spectral pattern is different for FIR and low-frequency Raman (and OKE) spectra for a given ionic liquid. Molecular dynamics simulations have shown that the density of vibrational states resembles low-frequency Raman and OKE spectra of ionic liquids. The group of Balasubramanian attempted a theoretical approach for understanding the low-frequency vibrations of nonprotic imidazolium and protic ammonium ionic liquids. These authors used quantum chemistry calculations of ion pairs and computer simulations of liquid and crystalline phases by classical (force field based) and ab initio MD simulations. The vibrational analysis by MD simulations has been performed by a normal-mode analysis after diagonalization of the Hessian matrix obtained from quenched configurations and also by Fourier transforming the time correlation function of atomic velocities. The density of vibrational states resulting from MD simulations exhibits the trend of higher frequency shift with increasing strength of anion–cation interactions in imidazolium or the number of hydrogen-bonding sites in ammonium ionic liquids. In the case of protic trialkylammonium trflate ionic liquids, $\text{N}^+\text{H}^+\cdot\cdot\cdot\text{O}^-$ stretching modes calculated around 160 cm$^{-1}$ agree with FIR spectra. However, the peaks in the theoretical density of vibrational states are found at significantly lower frequencies than in the experimental FIR spectra. The density of states calculated by MD simulation is more like the low-frequency Raman than the FIR spectrum. In other words, even though polarizability fluctuations are not being taken into account in the density of states, it resembles the representation of low-frequency Raman spectra of ionic liquids. Nevertheless, the calculations point out that the vibrational frequency of intermolecular dynamics is dominated by short-range interactions, and the peak position is indeed modulated by the strength of anion–cation hydrogen bond.

However, the actual mode composition involves a large number of atoms rather than being localized only in the C–H–A moiety. Furthermore, the density of states calculated by MD simulation of the liquid phase of $[\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{N}_2]^+\text{PF}_6^-$ resembles an envelope over the corresponding density of states of the crystalline phase, a finding in line with the previous proposition of Buffeteau et al. in their FIR study of ionic liquids. At this point we reach the application of vibrational spectroscopy in studying phase transitions of ionic liquids, an issue to be discussed in the next section.

The MD simulations of Balasubramanian et al. aimed to the analysis of atomic displacements of low-frequency vibrations by the calculation of time correlation function of ionic velocities, rather than time correlation functions of dipole moment or polarization fluctuation. In contrast, Hu et al. calculated time correlation function of polarizability by MD simulation of 1-methoxyethylpyridinium diacynamide aiming a direct comparison with a previous OKE spectroscopy study by Shirotia and Castner. The calculations of Hu et al. considered polarization fluctuations arising from reorientational dynamics and interaction-induced mechanism according to the dipole–dipole correlated (DID) model in analogy with the large body of literature on MD simulations of properties of spectroscopic interest in molecular liquids. It is worth noting that depolarization ratio as low as 0.1 in Raman spectra of high temperature molten salts prompted Madden et al. to propose other interaction-induced mechanisms resulting in polarization fluctuation (e.g., short-range overlap, field, and field gradient). In the case of ionic liquids, including reorientation and DID mechanism is consistent with the depolarization ratio of 0.75 found in low-frequency Raman spectra. Reorientational and DID mechanisms in low-viscous molecular liquids account for long- and short-time parts, respectively, of the time correlation function of polarizability fluctuation. In other words, DID mechanism is expected to manifest higher-frequency dynamics of molecules rattling in the cage of neighbors. It is known that a clear time or frequency separation between reorientational and interaction-induced dynamics might not be strictly valid even in molecular liquids (e.g., $\text{CS}_2$). Accordingly, Hu et al. found that interaction-induced contribution extends to a relatively long time of a hundred picoseconds because the cage effect and nondiffusive dynamics take longer in ionic liquids. On the other
Ionic liquid mesophases (i.e., liquid crystal) are formed with increasing length of the alkyl chain of cation or anion. 350,353,354 Among the first vibrational spectroscopy studies concerning ionic liquid phase transitions, De Roche et al. 355 used Raman spectroscopy to analyze the crystal at room temperature and the smectic phase at 353 K of \([\text{C}_4\text{C}_1\text{im}]\)[PF_6]. By using as vibrational probes the Raman bands at 1055, 1065, and 1119 cm\(^{-1}\), related to \(\nu_{\text{CC}}\) and \(\nu_{\text{C}}\) modes, they concluded that the hexadecyl chain is in the anti conformation for all of the dihedrals in the crystalline phase and the crystal melts with formation of the mesophase and occurrence of gauche conformers. There are interesting questions concerning ionic liquid crystals, 356 but we will focus in this review on phase transitions of medium size alkyl-chain ionic liquids, which usually have low melting points. 357

A recurrent issue addressed by vibrational spectroscopy studies of ionic liquid phase transitions is eventual conformational changes indicated by the characteristic bands of different conformers. The possibility for the ions acquiring different conformations can lead to crystal polymorphism and solid–liquid transitions due to interchange between conformers. 358 Hayashi et al. 181 characterized two crystal polymorphs of \([\text{C}_4\text{C}_1\text{im}]\)Cl by a combined analysis of X-ray powder patterns and Raman spectra. Soon after this work, Ozawa et al. 182 used Raman spectroscopy and DFT calculations to show that the rotational isomerism of the butyl chain of \([\text{C}_4\text{C}_1\text{im}]\) implies crystal polymorphism, one phase composed by anti–anti and the other one composed by gauche–anti conformers (see Figure 20 for the characteristic Raman bands of \([\text{C}_4\text{C}_1\text{im}]\) conformers). In a chapter of a recently published book, 236 Hamaguchi and coauthors reviewed their Raman spectroscopic studies on structure and phase transitions of imidazolium-based ionic liquids. Endo et al. 195,357–359 extended the analysis of phase transitions to \([\text{C}_4\text{C}_1\text{im}]\) based ionic liquids with different anions using Raman spectroscopy along other experimental techniques, such as NMR and differential scanning calorimetry (DSC). They reported the formation of three crystalline phases with \([\text{C}_4\text{C}_1\text{im}]\) having anti–anti, gauche–anti, and gauche′–anti conformations. Raman spectra and DFT calculations reported by Endo et al. 191 indicated the occurrence of two conformers, asymmetric and symmetric, for 1-isopropyl-3-methylimidazolium, \([\text{i-C}_4\text{C}_1\text{im}]\), in the liquid phase. However, crystalline phases of \([\text{i-C}_4\text{C}_1\text{im}][\text{Br}]\) and \([\text{i-C}_4\text{C}_1\text{im}][\text{Cl}]\) contain only the asymmetric conformer. 198 Endo et al. also found similar behavior of solid–solid transitions and cation conformational changes when methylation in the C(2) atom of the imidazolium ring lead \([\text{C}_4\text{C}_1\text{im}]\) to \([\text{C}_4\text{C}_1\text{C}_1\text{im}]\) based ionic liquids. Other systems for which temperature-dependent Raman spectroscopy was used to reveal conformational changes accompanying crystal polymorphism and solid–solid transition included piperidinium 132 and ammonium ionic liquids. 357

Turning now to conformational changes of the anion, Raman and IR spectra have been used to characterize the \([\text{NTf}_2]^{-}\) conformation along phase transitions of \([\text{NTf}_2]^{-}\) based ionic liquids. It is worth mentioning that before ionic liquids becoming a broadly investigated class of compounds, vibrational spectroscopy has been extensively used for studying \([\text{NTf}_2]^{-}\) in cisoid or transoid conformations (see Figure 12 for the characteristic Raman bands of \([\text{NTf}_2]^{-}\) conformers). 358 Castriota et al. 114 reported one of the first vibrational studies 359

![Figure 38](image-url)
Review

on temperature-dependent phase transition of a [NTf₂]⁻ based ionic liquid, namely [Pyr₄⁺][NTf₂], and its mixture with Li[NTf₂]. Raman spectroscopy provided insight about interactions between [NTf₂]⁻ and [Pyr₄⁺] and Li⁺ cations in crystal and liquid phases, but [NTf₂]⁻ conformation was not an issue. Herstedt et al. measured the temperature dependence of [NTf₂]⁻ Raman bands. The analysis helped understanding the disorder caused by [NTf₂]⁻ anion in the solid, thus explaining the formation of plastic crystals and, in part, accounting for the low melting point of [NTf₂]⁻ ionic liquids. Martellini et al. used Raman spectroscopy to follow the evolution of [NTf₂]⁻ conformation as a function of temperature in bulk and nanoconfined ionic liquids with protic and aprotic cations. Some studies also considered IR spectra as a function of temperature to follow [NTf₂]⁻ conformational changes during phase transitions. Vitucci et al. suggested that the longer alkyl chain in ammonium ionic liquids stabilizes the lower energy cisoid [NTf₂]⁻ conformer in solid phase because of stronger interactions between [NTf₂]⁻ and the polar head of the cation. It became apparent from vibrational spectroscopy studies that structural rearrangements in polar and nonpolar domains during phase transitions may be independent of each other. The [N(SO₂F)₂]⁻ is another anion for which conformational analysis in low temperature phase behavior was investigated by Raman spectroscopy. Shimizu et al. found two different crystalline phases for [Pip₄⁺][N(SO₂F)₂], [N(SO₂F)₂]⁻ in the cisoid or transoid conformation (see Figure 14 for the characteristic Raman bands of [N(SO₂F)₂]⁻ conformers). Kinetic effects play a central role in determining the complex phase behavior of ionic liquids. Lassègues et al. reported Raman spectra of [C₄C₁im]Cl in the crystal phase at 113 K obtained after slow cooling (~1 K min⁻¹) and glassy phase at 113 K obtained after fast cooling (~20 K min⁻¹). These authors found that the crystal phase contained the cisoid [NTf₂]⁻ conformer, whereas the glassy phase contained mainly the transoid conformer. The cooling-rate dependence of [NTf₂]⁻ conformation illustrates how the thermal history determines the ionic liquid phase behavior. In fact, Raman spectroscopy indicates that [NTf₂]⁻ achieves different conformations when partial crystallization of [C₄C₁im][NTf₂] is obtained by slow cooling or by cold crystallization (i.e., crystallization by heating the glassy phase). The Raman spectra of [C₄C₁im][NTf₂] shown in Figure 39 indicate there is mixture of [NTf₂]⁻ conformers in the normal liquid phase, whereas the cisoid or transoid conformation is obtained in the crystal formed by slow cooling or cold crystallization, respectively. Many ionic liquids are easily supercooled, exhibiting glass transition typically around 190–210 K, so that it might be difficult to obtain the low-temperature crystal. Crystalline phase has never been obtained for some ionic liquids along cooling, or it has been obtained only by the cold crystallization process. The ionic liquid can also become partially crystallized forming the so-called glacial state (i.e., microcrystallites immersed in a matrix of supercooled liquid), for instance, [C₄C₁im][NTf₂]. A large number of studies using DSC, NMR, and Raman spectroscopy have investigated the slow dynamics during the melting process of ionic liquids. Hamaguchi and Ozawa followed the melting of [C₄C₁im]Cl crystal by the time dependence of Raman bands which characterize different conformations of the butyl chain. They observed an unusually long time for equilibration of anti/gauche conformers in the liquid phase, concluding that conformational interconversion happens along slow collective transformation of ensembles of [C₄C₁im]⁺ cations. In a subsequent paper, the melting process of [C₄C₁im]Cl was investigated by Okajima and Hamaguchi using simultaneously the lattice vibration bands in the low-frequency range and the Raman bands of butyl chain conformers. Figure 40 taken from their work shows Raman spectra of [C₄C₁im]Cl during the melting process and Raman intensities as a function of time for the lattice vibration at 111 cm⁻¹ and the characteristic bands of butyl chain conformation. In this experiment, a small piece of [C₄C₁im]Cl single crystal was rapidly heated to 363 K, that is 30 K higher than the melting point. The low-frequency Raman spectrum of liquid [C₄C₁im]Cl has the typical quasi-elastic scattering (see section 5), whereas the crystal phase spectrum has peaks characteristic of lattice modes. Lattice modes gradually disappear during melting, while the quasi-elastic scattering intensity increases. However, the bottom panel of Figure 40 indicates time lag between the disappearance of lattice modes and the equilibration of anti/gauche population in the liquid phase. Thus, conformers remain in local structures, and only after conversion of those arrangements as a whole is the melting process completed. Endo and Nishikawa have also observed that conformational changes are linked to the melting process of [C₄C₁im]Cl, concluding that the premelting region observed in DSC as broad peaks corresponds to an equilibrium state distinct from liquid and crystalline states. Altogether, the kinetics of ionic liquids during crystallization or melting processes has been assigned to complex conformational changes depending on cooperative rearrangements and a sluggish collective dynamics. Vibrational spectroscopy has been used more recently to investigate crystallization, solid–solid, and glass transition of ionic liquids under high pressure. In analogy with temperature-dependent studies, Raman and IR spectra provide insights on conformational changes accompaniying high pressure phase transitions. These studies concerned mainly anti/gauche conformations of 1-alkyl-3-methylimidazolium cations, but some studies also analyzed conformations...
of ammonium cations \( \text{128, 235, 391, 392} \) and the \( \text{[NTf}_2\text{]}^- \) anion.\text{128, 364, 385, 393, 394} Many of these papers report the glass transition pressure at room temperature, \( P_g \) according to the method of measuring the pressure dependence of the bandwidth of ruby fluorescence spectrum.\text{395} Stress relaxation\text{317} is no longer achieved when the glass transition takes place, so that the ruby acts like a microscopic probe of stress heterogeneity in the sample. Thus, the plot of the bandwidth of ruby fluorescence spectrum as a function of pressure exhibits a noticeable change in slope at \( P_g \). The \( P_g \) of 1-alkyl-3-methylimidazolium-based ionic liquids depends on the alkyl chain length. For instance, \( P_g \) ranges from ca. 3.0 to 2.0 GPa along the series \([\text{C}_n\text{C}_1\text{im}][\text{BF}_4]\), as \( n \) increases from 2 to 8.\text{386}

The anion also plays a role in determining the glass transition under high pressure, for instance, \( P_g \) is 1.6 and 2.1 GPa for \([\text{C}_3\text{C}_1\text{im}][\text{PF}_6]\) and \([\text{C}_3\text{C}_1\text{im}][\text{BF}_4]\), respectively.\text{396} Interestingly, plots of the ruby emission bandwidth eventually suggests that other transitions take place for pressures higher than \( P_g \). Yoshimura et al.\text{386} proposed the formation of other densified structures most probably related to dynamic heterogeneity with the intrinsic hierarchy of structures relaxing at different time scales. However, this is an open issue which deserves further studies.

Some ionic liquids in glassy phase at high pressure experience\text{390} crystallization when decompessed, this finding being the pressure counterpart of cold crystallization when the low-temperature glass is heated.\text{386, 395} Kinetic of high pressure phase transition also exhibits similarities with low-temperature transition. It has been found that \([\text{C}_3\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]\) and \([\text{C}_4\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]\) may become a glass or a crystal depending on the compression rate.\text{387, 388} Moreover, large hysteresis of vibrational frequency and bandwidth of the high-pressure \([\text{C}_3\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]\) crystal was found when the pressure was released stepwise back to the atmospheric pressure.\text{387}

Raman spectroscopy has been used to show that high pressure crystallization of the protic ionic liquid \([\text{C}_3\text{NH}_3\text{][NO}_3]\) may result in a microscopically heterogeneous sample.\text{355, 392} Figure 41A shows two spectral patterns recorded by focusing the laser beam in different regions of the same sample inside the DAC after a quick increase of pressure to ca. 2.0 GPa. (Compare with the \( \nu(\text{NO}_3) \) Raman band of \([\text{C}_3\text{NH}_3\text{][NO}_3]\) in the normal liquid phase shown in Figure 34.) A photograph of the sample chamber with the \([\text{C}_3\text{C}_1\text{im}][\text{NO}_3]\) crystal is shown in Figure 41B. The distorted arrangement of hydrogen-bonded ions resulting in a distribution of \( \nu(\text{NO}_3) \) vibrational frequencies in liquid \([\text{C}_3\text{NH}_3\text{][NO}_3]\) was reproduced by DFT calculation of a cluster of four imionic pairs.\text{235} Thus, distinct local structures can be arrested in isles of microscopic heterogeneity under high pressure, resulting in the anomalous crystallization of \([\text{C}_3\text{NH}_3\text{][NO}_3]\).\text{326} The micro-Raman imaging in Figure 41C illustrates the spatial distribution of microscopic heterogeneity of the high-pressure \([\text{C}_3\text{NH}_3\text{][NO}_3]\) crystal. It is worth mentioning that stepwise increase of pressure to 1.5 GPa also generates the microscopic heterogeneity, and the actual \( \nu(\text{NO}_3) \) band shape depends on the rate of increasing pressure.\text{335, 392} Concerning crystal growth under high pressure, it is usually verified heterogeneous nucleation starting up from the gasket wall in the DAC sample chamber. We provide as a movie showing the crystallization process of \([\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]\) inside the DAC at ca. 1.0 GPa.

Magnetic ionic liquids are composed of metal-containing anions with magnetic behavior, \([\text{FeCl}_4]\) being the most common. Garcia-Saiz et al.\text{399} performed magnetization and magnetic Raman spectroscopy studies of \([\text{C}_3\text{C}_1\text{im}][\text{FeCl}_4]\) under high pressure. They found that the relatively low applied pressure of 0.34 GPa is enough to modify magnetic interactions and to induce transition from antiferromagnetic to ferromagnetic ordering. Furthermore, \([\text{C}_3\text{C}_1\text{im}][\text{FeCl}_4]\) exhibits magnetic hysteresis linked to liquid–solid phase transition due to the alignment of \([\text{FeCl}_4]\) anions.
Vibrational spectroscopy under high pressure allows one to obtain the volume of conformational change, $\Delta V$, in analogy to the temperature-dependent studies discussed in section 4.3.

One obtains $\Delta V$ from the pressure dependence of intensities of bands that characterize each conformer, $I_{\text{conf}}$. If one assumes that Raman scattering cross sections for conformers 1 and 2 do not depend on pressure then $\Delta V$ is given by

$$\Delta V = -RT \left[ \frac{\partial \ln (I_{\text{conf}}/I_{\text{conf}})}{\partial P} \right]_T$$

where $R$, $T$, and $P$ are the gas constant, temperature, and pressure, respectively. Takekiyo et al. determined $\Delta V(\text{planar} \rightarrow \text{nonplanar}) = +0.16 \text{ cm}^3/\text{mol}$ for $[C_4C_1im][BF_4]$ and $\Delta V(\text{anti} \rightarrow \text{gauche}) = -0.7 \text{ cm}^3/\text{mol}$ for $[C_2C_1im][BF_4]$. Capitani et al. obtained $\Delta V(\text{transoid} \rightarrow \text{cisoid})$ for the $[\text{NTf}_2^-]$ anion in $[\text{Pyt}_{11}][\text{NTf}_2]$ and $[\text{N}_{1116}][\text{NTf}_2]$, respectively, $\Delta V = 0.34$ and $-0.41 \text{ cm}^3/\text{mol}$. In the case of $[\text{N}_{1116}][\text{NTf}_2]$, Capitani et al. obtained $\Delta V(\text{transoid} \rightarrow \text{cisoid})$ from IR spectra, and they also obtained $\Delta V(\text{transoid} \rightarrow \text{cisoid}) = +0.7 \text{ cm}^3/\text{mol}$ in a linear regime for pressures higher than $P_g$ (i.e., above 2 GPa). These authors also obtained $\Delta H$ for $[\text{N}_{1116}][\text{NTf}_2]$ by temperature-dependent spectroscopy, and they discussed the competition between anion–cation interactions, relative energy of conformers, and the anion volume.

The low-frequency range probing lattice dynamics is of course expected to be very sensitive to ionic liquid phase transitions. As discussed in section 5, the low-frequency Raman spectra of amorphous phases exhibit the intense quasi-elastic scattering and the intermolecular vibrations appear as a broad band, the so-called boson peak, in contrast to the sharp peaks of crystal lattice modes. Figure 42 illustrates low-frequency Raman spectra at different temperature and pressure conditions for $[C_4C_1im][CF_3SO_3]$ as it undergoes glass transition or crystallization. The quasi-elastic scattering dominates the Raman spectrum for the normal liquid phase at 0.1 MPa and 298 K. The Raman spectrum of the glassy phase observed by sudden increase of pressure (2.4 GPa, 298 K) exhibits the boson peak at $\sim 21 \text{ cm}^{-1}$ and the imidazolium ring librational mode at $\sim 140 \text{ cm}^{-1}$. The high-pressure crystal (1.3 GPa, 298 K), with consequent sharp bands in the Raman spectrum, is obtained when pressure is stepwise increased. $[C_4C_1im][CF_3SO_3]$ always crystallizes at low temperature under usual cooling rates, and the spectral pattern of the crystal at 0.1 MPa and 230 K does not resemble the pattern of the high-pressure crystal. However, a direct qualitative interpretation of different crystal structures based only on the low-frequency vibrational spectrum has to be done with care. Chen et al. obtained single-crystal X-ray diffraction data for a series of nitrile functionalized ionic liquids and analyzed low-frequency Raman spectra taking into account the crystal structures. They found that ionic liquids having the same space group exhibit indeed similar low-frequency Raman spectra, but they also warned that the analysis based only on the similarity of Raman spectra might lead to erroneous conclusions and it should be complemented by X-ray diffraction measurements.

Few works concerning ionic liquid phase transitions have been published using the low-frequency range of vibrational spectra. Roth et al. discussed the effects of hydrogen bonds in FIR spectra of $[\text{NTf}_2^-]$-based systems with a series of imidazolium cations with the ring hydrogen atoms substituted by methyl groups, including the solid phase of 1,2,3,4,5-pentamethyldimidazolium derivative, whose melting point is 391 K. Low-frequency Raman spectroscopy has been used by Okajima and Hamaguchi in order to follow the melting process of $[C_4C_1im][\text{Cl}]$ (see Figure 40) and by Faria et al. to distinguish crystalline phases of $[C_6H_5NH_2][\text{NO}_3]$ at different conditions of temperature and pressure. The low-frequency range of the Raman spectrum of $[C_4C_1C_1C_1N][\text{NTf}_2]$ also indicated the glacial state (i.e., mixture of microcrystals and supercooled liquid), according to the occurrence of sharp bands of lattice modes on top of the broad band characteristic of amorphous phase. The ionic liquids $[C_4C_1C_1C_1N][\text{NTf}_2]$ and $[C_4C_1C_4C_4N][\text{NTf}_2]$ do not crystallize under high-pressure at room temperature, instead they undergo glass transition at 1.1 and 1.3 GPa, respectively. Accordingly, the low-frequency Raman spectrum under high-pressure exhibits low intensity of quasi-elastic scattering and the characteristic boson peak due to intermolecular dynamics as expected for a glassy phase. Penna et al. have found a correspondence between the position of intermolecular vibrational modes in the liquid state and the spectral features observed after partial crystallization of samples at low temperature or high pressure. This point is illustrated in Figure 43 with the susceptibility representation of the Raman spectra of $[C_4C_1im][\text{NTf}_2]$ in supercooled liquid and partially crystallized (230 K, black line) phases. The components (blue lines) used in the curve fit (red line) of the liquid spectrum seems to correspond to broadening of sharp bands of the crystal spectrum. This finding strongly suggests that there is some kind of mesoscopic order in the supercooled ionic liquid beyond the well-known nanoscale heterogeneity of polar/nonpolar domains. However, it is worth noting that in many cases, e.g. $[C_4C_1im][\text{Cl}]$, the broad bands in the low-frequency Raman spectrum of the glassy phase barely indicate any direct correspondence to the sharp peaks in the crystal parent spectrum.

It is natural that there are several open questions related to phase behavior of ionic liquids proper to the complexity of structural and kinetic aspects of the transitions under low pressure.
temperature or high pressure. Studies simultaneously changing
3344 temperature and pressure are on demand for covering a wider
3345 region of the phase diagram of ionic liquids. These
3346 investigations would go beyond the scope of ionic liquids by
3347 shedding light on more general issues, such as the interplay
3348 between glass transition and crystallization, nucleation and
3349 crystal growth processes, amorphous–amorphous transitions,
3350 and the melting process. Moreover, the mixture of ionic liquid
3351 with other compounds can produce hybrid materials with
3352 interesting properties and phase transitions. For example, Abe
3353 et al.401 used Raman spectroscopy in studying confinement of
3354 water in an ionic liquid and the concentration dependence of
3355 phase behavior. Furthermore, crystallization of ionic liquid from
3356 different solvents might be an efficient method for purification
3357 and to generate new crystalline phases, as shown by Li et al.383
3358 for an ionic liquid–methanol solution under high pressure. IR
3359 and Raman spectroscopies are powerful tools for addressing
3360 many of these issues.

7. VIBRATIONAL SPECTROSCOPY OF IONIC LIQUID
3361 SOLUTIONS
3362
3363 An appealing feature of the ionic liquid chemistry is the
3364 possibility of fine-tuning the properties by proper combination
3365 of cations and anions or mixing different ionic liquids.402–404
3366 From the point of view of vibrational spectroscopy, mixtures of
3367 ionic liquids with other ionic liquids, molecular solvents, ions,
3368 polymers, etc. can serve as model systems for understanding the
3369 complex balance of intermolecular interactions determining
3370 solvent properties and the liquid structure. A large number of
3371 systems has been studied using vibrational spectroscopy, but in
3372 this section we limit our discussion to mixtures of ionic liquids
3373 with other ionic liquids, water, or other molecular solvents,
3374 gases, and salts. The examples given in this section show that
3375 attempts to get insights on intermolecular interactions from
3376 vibrational spectroscopy of ionic liquids rely on frequency shift,
3377 band broadening, intensities variation, etc. take place in the
3378 mixtures. The approach of assigning physically meaningful
3379 interpretation to spectral changes in Raman excess spectrocy-
3380 perty usually demands a reference spectrum. In Raman excess
3381 spectroscopy, or other excess spectroscopies, the deviation of
3382 the experimental spectrum of the mixture from the ideal
3383 counterpart, which is the weighted average of pure samples
3384 spectra, may provide chemical information about interactions in
3385 the mixture.405,406 However, this approach is undermined when
3386 the reference spectrum cannot be obtained. In this context,
3387 Koch et al.407 discussed a multivariate approach for quaternary
3388 mixtures of [C2C1im][C2SO4], water, and D- and L-glucose. A
3389 word of caution is in order since not all multivariate analysis
3390 methods will provide meaningful information in the first
3391 approach, a careful choice being fundamental for the employed
3392 method and proper data pre and post processing.408
3393 Hydrogen bonding in equimolar mixtures of ionic liquids has
3394 been studied by Fumino et al.409 using FIR spectroscopy. These
3395 authors performed an investigation of imidazolium-based ionic
3396 liquids with systematic methylation in the imidazolium ring
3397 while keeping the same [NTf2]− anion409 and also the mixture
3398 of ionic liquids with the same triethylammonium cation and
3399 methylsulfate and triflate anions.410 The underlying assumption
3300 in this approach is the additivity of spectra of different ionic
3301 liquids, an issue which has been discussed mainly using optical
3302 heterodyne-detected Raman-induced Kerr effect spectroscopy,
3411,315,412 and also using far infrared419 infrared
3412 spectroscopies. Cha and Kim414 considered the IR bands
3413 belonging to γ (CH), ν (C(2)−H), and νas (C(3,4,5)−H) modes to study hydrogen-bonding effects due to anion coordination in
3414 mixtures of regular C(2) deuterated [C2C1im] cation with 3415 different anions, Cl−, I−, [BF4]−, and [NTf2]−. If additivity were
3416 valid, the spectrum of the mixture would be the sum of spectra
3417 of the neat liquids weighted by the concentration. The
3418 agreement between the actual spectrum of the mixture and the
3419 concentration-simulated spectrum for [C2C1im]/[C2C1im]Cl and
3420 [C2C1im]/[C2C1im]BF4 indicated that cation–anion interactions were not significantly changed upon mixture.403
3421 The same conclusion is valid for [C2C1im]/[BF4] Cl− and [C2C1im]/[BF4] mixture.414 Aparicio and Attilhan415 also concluded for
3422 additivity of IR spectra in mixtures of 1-butyl-3-methylpyridinium, [Py1,4][BF4], and 1-oxyl-3-methylpiridinium, [Py1,4][BF4], with the [BF4]− anion. In contrast, in deuterated [C2C1im]+
3423 mixtures of [NTf2]− with either Cl− or I−, the hydrogen
3424 bond imposed by the more coordinating halide anion caused
3425 red shift of vibrational frequency of the ν (C(2)−D) mode and
3426 change in dipole moment derivative as inferred by the
3427 dependence of band area with concentration.414 Analogous
3428 effect of mixing anions with different coordination strength has
3429 been found by Fumino et al.410 in mixtures of protic
3430 imidazolium ionic liquids. Aparicio and Attilhan415 found
3431 nonlinear concentration dependence of vibrational frequencies
3432 of C−H stretching modes in the range of 2800–3200 cm−1 for
3433 [Py1,4][BF4]/[Py1,4][N(CN)2] mixtures. This finding has been attributed to structural changes and dominance of [N(CN)2]− 420 interaction, a conclusion being corroborated by molecular
3434 dynamics simulations. Miran et al.416 found anion effects in IR
3435 spectra of mixtures of protic trimethylammonium ionic liquids with [NTf2]− and [HSO4]−. Therefore, one finds significant
3436 spectral signatures in mixtures of ionic liquids, in particular
3437 involving different anions, when there is large difference in
3438 coordinating and hydrogen bonding abilities of the ions.427
3439 Furthermore, the different coordination capacity of anions
3440 results in different chemical environments,410 as also suggested
3441 by the NMR measurements of the work of Cha and Kim.430
3442
3443 Even though mixtures of cations with different lengths of the
3444 alkyl chain (e.g., 1-alkyl-3-methylimidazolium cations), but the
3445 same anion, implies only small effects on vibrational spectra in
3446 comparison with spectra of the parent neat liquids, the
3447 transport coefficients, excess thermodynamic properties, and
3448

Figure 43. Low-frequency Raman spectra in the susceptibility
representation of [C2C1im][NTf2] in supercooled liquid phase (250
K, ●) and after crystallization (230 K, black line). The curve fit (red
line) and the individual components of fit (blue lines) of the
supercooled liquid spectrum are shown. Reproduced with permission
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Mixtures of ionic liquids with molecular solvents have been used to probe intermolecular interactions and structure, transport properties, phase transitions, and excess thermodynamic properties. Vibrational spectroscopy may address structural features such as nanoscale segregation, solvent properties and ionic liquid polarity, and intermolecular interactions (e.g., the role played by hydrogen bonding). In line with this finding, Bodo et al. also observed a slight blue shift of vibrational modes related to the alkyl chain and the polar head in the Raman spectra of \([\text{C}_6\text{H}_4\text{N}_2\text{H}_10\text{][NO}_3\text{]}\) protic ionic liquid in mixtures with water.

Danten et al. carried out a systematic study of \([\text{C}_6\text{H}_4\text{N}_2\text{im}\text{]}\) with increasing length of the alkyl chain (n = 1, 2, 4, 8), with \([\text{BF}_4\text{]}\) and \([\text{PF}_6\text{]}\), for water content below the limit of solubility in these ionic liquids. These authors used IR and Raman spectroscopies in combination with ab initio calculations for a nearly symmetrical complex made of one water molecule and two anions. The experimental difference of ca. 70–80 cm\(^{-1}\) between symmetric and antisymmetric OH stretching vibrations was reproduced by the calculations of such complexes, but they did not find any significant effect of the alkyl chain length on the vibrational spectra of the mixtures.

The enthalpy of vaporization of water molecules from the bulk of the ionic liquid was estimated from the vibrational frequency shift of the antisymmetric stretching mode and resulted in the following order for the water–anion interaction strength:

\[
\text{[PF}_6\text{]}^- < \text{[BF}_4\text{]}^- < \text{[NTf}_2\text{]}^- < \text{[ClO}_4\text{]}^- < \text{[CF}_3\text{SO}_3\text{]}^- < \text{[NO}_3\text{]}^- < \text{[CF}_3\text{CO}_2\text{]}^- < \text{[SbF}_6\text{]}^-.
\]

The enhancement of the asymmetric stretching mode intensity of water molecule in ionic liquids and in some electrolytic solutions has been found. Danten et al. evaluated the anion dependence of this spectral feature in \([\text{C}_6\text{H}_4\text{N}_2\text{im}\text{]}\) ionic liquids, keeping the water content below the respective solubility. Using IR, Raman, and ab initio calculations, they showed that the “interaction hierarchy” for anions with water is \([\text{PF}_6\text{]}^- < [\text{BF}_4\text{]}^- < [\text{NTf}_2\text{]}^- < [\text{ClO}_4\text{]}^- < [\text{CF}_3\text{SO}_3\text{]}^- < [\text{NO}_3\text{]}^- < [\text{CF}_3\text{CO}_2\text{]}^- < [\text{SbF}_6\text{]}^-.

The trend in interaction energy has the correspondence in distances between water and the fluorine atoms on the calculated clusters, 1.84 and 1.72 Å in \([\text{PF}_6\text{]}^-\) and \([\text{BF}_4\text{]}^-\), respectively, or the oxygen atoms of the anions, 2.0 and 1.9 Å in \([\text{NTf}_2\text{]}^-\) and \([\text{CF}_3\text{SO}_3\text{]}^-\), respectively.

Dahi et al. studied the water sorption isotherms and ATR spectra of several ionic liquids with the protic cations \([\text{C}_6\text{H}_4\text{N}_2\text{H}_10\text{]}\) and \([\text{C}_6\text{H}_4\text{N}_2\text{im}\text{]}\) and the nonprotic \([\text{C}_4\text{H}_10\text{N}_2\text{H}_10\text{]}\) and \([\text{C}_4\text{H}_10\text{N}_2\text{im}\text{]}\) with anions \([\text{PF}_6\text{]}^-\), \([\text{BF}_4\text{]}^-\), \([\text{CF}_3\text{SO}_3\text{]}^-\), dibutylphosphate, and bis(2-ethylhexyl)phosphate. These authors found a small effect.

There are other spectral changes when ionic liquids are mixed with water besides those modes involving the hydrogen atoms of the imidazolium ring. Saha and Hamaguchi found all anti conformation of the butyl chains in \([\text{CN}-\text{C}_4\text{H}_10\text{N}_2\text{im}\text{][Cl}\) and \([\text{CN}-\text{C}_4\text{H}_10\text{N}_2\text{im}\text{][Br}\) crystals, but the intensities of Raman bands belonging to the gauche conformer increase when the crystals were exposed to water. Proper to the appearance of a Raman band at 3300 cm\(^{-1}\) assigned to OH stretching mode, they also suggested that water molecules make a tight hydrogen bond network with the anions, displacing them from their original equilibrium position.

Raman spectroscopy indeed indicates that the population of gauche conformer increases upon the anti conformer when a \([\text{C}_4\text{H}_10\text{N}_2\text{im}\text{]}\) based ionic liquid is diluted in water. Jeon et al. also observed that the population of gauche increases with respect to the anti conformer as the water content increases, but the conformers population ratio decreases again beyond ca. 45 mol L\(^{-1}\). These authors attributed the increase in vibrational frequencies of \(v(CH_2)\) and \(v(CH_3)\) modes of the alkyl chain to interactions, which are mainly repulsive in nature, with the oxygen atoms of water. In line with this finding, Bodo et al. also observed a slight blue shift of vibrational modes related to the alkyl chain and the polar head in the Raman spectra of \([\text{C}_6\text{H}_4\text{N}_2\text{H}_10\text{][NO}_3\text{]}\) protic ionic liquid in mixtures with water.

In order to record Raman spectra of glassy \([\text{C}_2\text{H}_4\text{N}_2\text{im}\text{][NTf}_2\text{]}\) at low temperature, Penna et al. added a small amount (10% mol) of \([\text{C}_6\text{H}_4\text{N}_2\text{im}\text{][NTf}_2\text{]}\) to prevent crystallization of \([\text{C}_2\text{H}_4\text{N}_2\text{im}\text{][NTf}_2\text{]}\). This allowed studying the characteristic boson peak in the low-frequency Raman spectra of glassy \([\text{C}_2\text{H}_4\text{N}_2\text{im}\text{][NTf}_2\text{]}\), \([\text{C}_2\text{H}_4\text{N}_2\text{im}\text{][NTf}_2\text{]}\), and \([\text{C}_2\text{H}_4\text{N}_2\text{im}\text{][NTf}_2\text{]}\). The boson peak frequency does not depend on the chain length, instead the frequency depends on the strength of the anion–cation interaction when the anion is changed while keeping the same cation.
of the alkyl chain length of the cation for the same anion and whether the cation is protic or not. They also show that characteristic IR bands of free water do not appear in the spectrum of \([\text{C}_2\text{NH}_3][\text{CF}_3\text{SO}_3]\), suggesting that water molecules are part of a hydrogen bond network even at low concentrations so that vibrational frequencies of symmetric and asymmetric modes are the same as in liquid water. There is a strong dependence of the \(\nu(C=O)\) mode of \([\text{CF}_3\text{SO}_3]^-\) with the water activity, in contrast to \([\text{PF}_6]^-\), \([\text{BF}_4]^-\), and \([\text{NTf}_2]^-\), whose vibrational frequencies are only weakly concentration-dependent. Strong dependence of anion vibrational frequencies with the amount of water has also been reported for \([\text{CH}_3\text{COO}]^-\), \([\text{CF}_3\text{COO}]^-\), \([\text{NO}_3]^-\), and \([\text{C}(\text{CN})_3]^-\).

The ab initio calculations at the DFT/B3LYP level of theory performed by Danten et al.\(^{43}\) for the water-[C\(_2\)C\(_1\)im][NTf\(_2\)] system considered a 1:2 complex with the [NTf\(_2\)]\(^-\) in the cisoid conformation. The anion–water conformation and stoichiometry they used, however, were contrary to previous results. Yaghini et al.\(^{44}\) found that the anion conformation does not change upon addition of water (recall that in pure [C\(_2\)C\(_1\)im]-[NTf\(_2\)]) and [C\(_2\)C\(_1\)im][NTf\(_2\)] the transoid conformation is preferred, see section 4.3). Moreover, Wulf et al.\(^{45}\) pointed out that [NTf\(_2\)]\(^-\) is unlikely to form 1:2 complex with water due to steric reasons. When the 1:2 water–anion complexes are considered in order to represent solutions of low-water concentration,\(^{429,433,442,443,386}\) the calculations should also include two cations to take into account five body nonadditive interactions.\(^{442,443}\)

High concentration of water seems to disrupt the nanoscale segregation of polar/apolar domains in liquid ions.\(^{446}\) In the case of intermediate water concentration, some authors claim that the system is homogeneous without phase segregation, but others argue in favor of formation of water clusters. If the water content in N,N-diethyl-N-methyl-2-methoxyethylammonium tetrafluoroborate is below 80% (mol), it has been proposed that water is mostly confined since Raman frequencies of symmetric and asymmetric modes are close to the values of free water molecules.\(^{401,446}\) The limit value of 80% is related to the ability of forming 1:4 [BF\(_4\)]\(^-\)–water complexes, and beyond that, water starts to interact with the more electronegative part of the cation. The OH stretching modes appear in the spectral range of \([\text{C}_2\text{NH}_3][\text{CF}_3\text{SO}_3]\), suggesting that water starts to interact with the more electronegative part of the cation. The OH stretching modes appear in the spectral range of \([\text{C}_2\text{NH}_3][\text{CF}_3\text{SO}_3]\), suggesting that water starts to interact with the more electronegative part of the cation. The OH stretching modes appear in the spectral range of \([\text{C}_2\text{NH}_3][\text{CF}_3\text{SO}_3]\), suggesting that water starts to interact with the more electronegative part of the cation.
imidazolium ring, specifically the $\nu_C(C(6)\cdots H)$, in line with similar results obtained by Pal et al.\textsuperscript{452} The $\nu_S(S\cdots O)$ and $\nu_C(C(21)\cdots H)$ modes also exhibit frequency shifts in the case of ionic liquids containing $[BF_4^-]$, it has been proposed that regions rich in either ethylene glycol or ionic liquid are formed.

Furthermore, Singh et al.\textsuperscript{452} used the blue shift of $\nu(OH)$ in order to make qualitative inference about the extent of disturbance of the hydrogen bond network of ethylene glycol.

Comparatively, the effect is larger for $[C_4C_1im][C_1SO_4]$ and in the case of $[BF_4^-]$ based ionic liquids, the disturbance of the hydrogen bond network of ethylene glycol is larger as the alkyl chain is longer. Pal et al.\textsuperscript{452} suggested that the interaction that causes frequency shift of $\nu_C(C(4)\cdots H)$ is of electrostatic nature, rather than hydrogen bonding between hydrogen atoms of the imidazolium ring and ethylene glycol. On the other hand, the fact that aggregation is not observed in the alkylsulfate-based ionic liquid might be assigned to the strong anion-ethylen glycol hydrogen bond. This finding is in line with conclusions from the IR study by Pal et al.,\textsuperscript{452} who used 1,2-propanediol as a probe in mixtures with $[C_4C_1im][C_1SO_4]$ and $[C_4C_1im][BF_4^-]$. They pointed out from ATR measurements that $[C_4SO_4^-]$ disturbs the most the hydrogen bond network of the alcohol, followed by $[NTf_2^-]$ and $[BF_4^-]$. It is worth noting that such order of "strength of disturbance" is somewhat similar to the interaction strength series proposed by Cammarata et al.\textsuperscript{459} and the polarity series obtained by Wulf et al.\textsuperscript{459}.

Shirato et al.\textsuperscript{453} and Shimomura et al.\textsuperscript{454} used IR spectroscopy, among other techniques, to study mixtures of benzene in imidazolium ionic liquids by following the effect of the ions on the vibrational frequency of the out-of-plane $C\cdots H$ bending mode, $\delta_{op}(CH)$, of benzene. They found a significant blue shift of $\delta_{op}(CH)$, and supported by structural data and quantum chemistry calculations, they suggested that the interaction between benzene and the imidazolium ring is stronger than interactions between benzene rings ($\pi\cdots\pi$ interactions) or between benzene and hydrogen atoms ($C\cdots H\cdots\pi$ interactions).

Along the comparison between $[C_2C_1im][BF_4]$ and $[C_4C_1im][BF_4^-]$, Shirato et al.\textsuperscript{453} assigned the larger frequency shift in the latter to weaker interaction between $[NTf_2^-]$ and the cation, allowing for stronger interaction between the probe molecule (benzene) and the cation. One could argue from the results of Shimomura et al.\textsuperscript{454} that the alkyl chain length plays a less important role because the vibrational frequency shift of $\delta_{op}(CH)$ is almost the same in the $[C_2C_1im][NTf_2^-]$-benzene mixture. It is worth mentioning that benzene-ionic liquid mixtures have been studied more often by OKE spectroscopy.\textsuperscript{205,453$^-$$^457$}

Vibrational spectra of different solutes have been used to probe the solvent ability of ionic liquids. Wülf et al.\textsuperscript{429} used water as a probe of solvent polarity of imidazolium ionic liquids with the anions $[SCN]^-$, $[N(CN)_2]^-$, $[C_1SO_4]^-$, and $[NTf_2^-]$.\textsuperscript{429}

Their method relies on measuring the redshift of vibrational frequencies of stretching modes of water, whose magnitude is then related to dielectric constant and different polarity parameters (e.g., the Kamlet–Taft solvatochromic parameters).\textsuperscript{406$^-$$^409$} The anion increases the ionic liquid polarity in the order: $[NTf_2^-] < [C_1SO_4]^- < [N(CN)_2]^-$ $< [SCN]^-$, while the length of the alkyl chain of imidazolium cations has negligible effect on polarity of the investigated ionic liquids.

Other molecules besides water have been used to probe ionic liquid polarity using vibrational spectroscopy. Tao et al.\textsuperscript{460} considered the (CO) mode of acetone, $N,N$-dimethylformamide, and Fe(CO)$_3$, as polarity probes. The authors did not provide parameters to quantify the polarity, but they showed qualitatively the correlation between the polarity and the vibrational frequency shift of (CO). Using acetone as a probe in ionic liquids with different anions, they showed that polarity of $[NTf_2^-]$ is smaller than $[SCN]$ based ionic liquids, in line with the conclusions drawn by Wülf et al.\textsuperscript{429} using water as a probe.\textsuperscript{429} The $\nu(CO)$ frequency of Fe(CO)$_3$, allowed the authors to propose a series of decreasing polarity as the alkyl chain length increases in $[C_4C_1im][BF_4]$, $3 \leq n \leq 10$, and $[C_4C_1im][PF_6]$, $3 \leq n \leq 6$. Garcia et al.\textsuperscript{461} used frequency shifts of $\nu(CN)$ and $\nu(CD)$ modes of normal and deuterated acetonitrile to estimate acceptor (AN) and donor (DN) numbers\textsuperscript{461} of ionic liquids on the basis of extensive data available for acetonitrile in common molecular solvents. It has been found consistent AN and DN values estimated from either $\nu(CN)$ or $\nu(CD)$ modes of acetonitrile. The observed trend is that fluorination of anions implies more acidic local environments (higher AN), while nonfluorinated anions implies more basic environments (higher DN).\textsuperscript{461} Summing up, the results of vibrational spectroscopy investigations of ionic liquids polarity indicate that the anion plays the dominant role, whereas the effect of changing the length of the alkyl chain of dialkylimidazolium cations is less important.

A well-known application of ionic liquids concerns their capacity to absorb gases. This can be a selective process aiming sample purification or gas capture to remove greenhouse gases from the atmosphere.\textsuperscript{403,404} Vibrational spectroscopy has been used as an analytical tool for quantifying the amount of absorbed gas\textsuperscript{42} or for studying the mechanism and eventual reactions between the gas molecules and ion species.\textsuperscript{32,463} Among the gas–ionic liquid solutions most widely investigated by vibrational spectroscopy, SO$_2$ and CO$_2$ are the gases which draw more attention proper to their impact on the environment.\textsuperscript{3786}

Zeng et al.\textsuperscript{464} carried out a systematic IR spectroscopy study of SO$_2$ absorption by pyridinium-based ionic liquids with different lengths of the alkyl chain, while keeping the same $[BF_4^-]$ anion, or different anions, $[SCN]^-$, $[BF_4^-]$, and $[NTf_2^-]$, while keeping the same $[Py_4]^+$ cation. In the case of $[Py_4][NTf_2]$, the authors did not observe the SO$_2$ bands after gas absorption because of overlapping with the $[NTf_2^-]$ bands at 1139 and 1352 cm$^{-1}$. The symmetric and antisymmetric O–O stretching modes of the SO$_2$ molecule, $\nu(SO)$ and $\nu(SO)$, are observed at 1149 and 1332 cm$^{-1}$ in $[Py_4][BF_4]$ and 1124 and 1299 cm$^{-1}$ in $[Py_4][SCN]$, respectively. The vibrational frequencies of $\nu(SO)$ and $\nu(SO)$ in pure liquid SO$_2$ are 1144 and 1336 cm$^{-1}$, respectively.\textsuperscript{42} Although Zeng et al.\textsuperscript{464} did not address the issue of vibrational frequency shift between pure liquid SO$_2$ and SO$_2$-ionic liquid solutions, it is worth noting that $\nu(SO)$ and $\nu(SO)$ exhibit shifts to opposite directions when SO$_2$ is dissolved in $[Py_4][BF_4]$ and a much larger red shift of both $\nu(SO)$ and $\nu(SO)$ in $[Py_4][SCN]$. Variation of the alkyl chain length of the pyridinium cation, while keeping the same $[BF_4^-]$ anion, has no effect on vibrational frequencies of SO$_2$ modes.\textsuperscript{3807}

Shang et al.\textsuperscript{465} and Huang et al.\textsuperscript{466} studied by IR spectroscopy the SO$_2$ absorption in ionic liquids containing tetramethylguanidinium cations and different anions. Huang et al.\textsuperscript{465} claimed there is no chemical absorption but only physical absorption when SO$_2$ is absorbed by $[TMGH][BF_4]$ or $[TMGH][NTf_2]$, as the only spectral feature is occurrence of 3813.
two $\nu_{d}(SO)$ modes, 1376 and 1360 cm$^{-1}$, observed in both ionic liquids. Shang et al.$^{465}$ dealing with the same [TMGHT]$^{-}$

cation, but the imidazolate, phenolate, and 2,2,2-trifluoroacetate anions, argued that new bands at ca. 1410 and 954 cm$^{-1}$ are due to $S$–0 and $S$–0–H groups, respectively. The latter band was also observed when SO$_2$ was dissolved in another imidazolate ionic liquid with the 1-(N,N-diethyliaminomethyl)-3-

methyliimidazoliodiazonium cation, so that the authors claimed that the mechanism of SO$_2$ uptake in these ionic liquids involves chemical absorption. Ando et al.$^{469}$ and Siqueira et al.$^{469}$ studied both the high- and the low-frequency spectral features of Raman spectra of [C$_4$C$_1$im][Br] after SO$_2$ absorption. Solid [C$_4$C$_1$im][Br] at room temperature melts upon absorption of SO$_2$. When SO$_2$ is absorbed by [C$_4$C$_1$im][Br], the relative intensities of Raman bands at ca. 600 and 620 cm$^{-1}$, which characterize gauche and anti conformers (see Figure 20), become more similar to that found in [C$_4$C$_1$im]I. Furthermore, vibrational frequency shifts of $\nu_5$(SO) and $\nu_4$(SO) modes were attributed to specific charge transfer interactions between SO$_2$ and Br$^-$. The proposed physical picture of shielding the cation–anion interactions after uptake of SO$_2$ was supported by molecular dynamics simulations.$^{468,469}$ The authors found good agreement between the density of states calculated by the Fourier transform of the autocorrelation function of velocity and that of density of states calculated by the density of states obtained from Born–Oppenheimer electron density. The latter is a weaker Lewis base than [PF$_6$]$^-$. Kazarian et al.$^{470}$ obtained ATR spectra of [Py$_4$][BF$_4$] at 40 $^\circ$C and 6.8 MPa. Splitting of the IR band belonging to the bending mode of CO$_2$ has been found. Such splitting of the band is due to the lifting of degeneracy, with the expectation that the splitting would be larger for solvents with more pronounced Lewis base character. Since the splitting was more pronounced in [C$_4$C$_1$im][BF$_4$] than [C$_4$C$_1$im][PF$_6$], Kazarian et al.$^{470}$ concluded that [BF$_4$]$^-$ is a stronger Lewis base than [PF$_6$]$^-$. Andanson et al.$^{471}$ characterized CO$_2$ solutions in [C$_4$C$_1$im][PF$_6$] under different CO$_2$ pressure at 40 $^\circ$C using ATR spectroscopy. The authors were able to estimate the swelling of the ionic liquid with increasing CO$_2$ pressure, the CO$_2$ diffusion within the ionic liquid, and solubility in [C$_4$C$_1$im][PF$_6$]. The vibrational spectrum of [C$_4$C$_1$im][PF$_6$] suggested only minor structural modifications after CO$_2$ uptake. The most significant effects of CO$_2$ absorption on the IR spectrum were the change in relative intensities of bands at 600 and 625 cm$^{-1}$, which characterize the relative proportion of gauche and anti [C$_4$C$_1$im]$^+$ conformers and frequency shift of the $\nu_5$(PF) mode of [PF$_6$]$^-$. Seki et al.$^{472}$ studied supercritical CO$_2$ dissolved in [C$_4$C$_1$im]$^+$ based ionic liquids with [PF$_6$]$^-$ and [NTf$_6$]$^-$, and [Py$_4$][BF$_4$], using ATR spectroscopy at 50 $^\circ$C and 12 MPa. In contrast to Kazarian et al.$^{470}$ Seki et al.$^{472}$ have not found splitting of the CO$_2$ bending mode in the CO$_2$ solution in [C$_4$C$_1$im][BF$_4$], arguing that the doublet coincides into a single band under higher CO$_2$ pressure. In the case of CO$_2$ solution in [Py$_4$][BF$_4$], no frequency shift of $\nu_5$(BF$_2$) modes was observed, whereas in [C$_4$C$_1$im][BF$_4$] there were frequency shifts of the cation $\nu_4$(C$_{4,5}$)–H mode and the anion $\nu_5$(BF$_2$) mode. Seki et al.$^{472}$ claimed that CO$_2$ interacts mainly with the [BF$_4$]$^-$ and that the new species formed CO$_2$-[BF$_4$]$^-$ is a stronger base than the single [BF$_4$]$^-$. Vibrational spectroscopy has been extensively used to study CO$_2$ absorption in imidazolium ionic liquids with the [CH$_3$COO]$^-$ anion. The mechanism of chemical absorption of CO$_2$ in [C$_4$C$_1$im][CH$_3$COO] based on the reaction between [CH$_3$COO]$^-$ and the C(2)–H acidic hydrogen atom of the imidazolium ring, leading to the formation of a carbene complex with CO$_2$, 1-butyl-3-
methylimidazolium-2-carboxylate, was verified through IR and Raman spectroscopies.$^{32,162}$ Formation of such carboxylate species leads to new bands in both the IR (ca. 792, 1323, and 1665 cm$^{-1}$) and Raman (ca. 794, 1323, and 1672 cm$^{-1}$) spectra. Figure 44 taken from the work of Cabaço et al.$^{462}$ indicates by arrows these IR and Raman appearing in the spectra of [C$_4$C$_1$im][CH$_3$COO] containing CO$_2$ or 13CO$_2$. Cabaço et al.$^{462}$ draws attention to the fact that, at molar fractions smaller than 0.3 (or CO$_2$ pressures of the order of 6 MPa), the spectra do not exhibit the Fermi dyad (i.e., the overtone of the CO$_2$ bending mode in Fermi resonance with the $\nu_5$(CO)).$^{475}$ This indicates that the CO$_2$ symmetry has been altered in [C$_4$C$_1$im][CH$_3$COO], whereas the Fermi dyad appears when CO$_2$ is dissolved in ionic liquids containing anions other than [CH$_3$COO]$^-$. Besides [CH$_3$COO]$^-$ based ionic liquids, there are reports of other anions with carbylate$^{474,476}$ or phenolate$^{477}$ groups which also favor mechanism of chemical absorption of CO$_2$. Furthermore, the vibrational dynamics of CO$_2$ in ionic liquids has also been studied by time-resolved IR spectroscopy.$^{378}$

Other important contexts for ionic liquid applications include electrochemistry and catalysis, in which they can be used as solvents for electrodeposition (or electroplating) of materials, electrolytes for batteries, etc. Dissolution of precursors or catalysts (e.g., AlCl$_3$, Al$_2$Cl$_7$, and NbCl$_5$) or ionic species (e.g., Li$^+$ and Na$^+$) may be studied using IR and Raman spectroscopies for a deeper understanding of solvation and structural modification of the ionic liquid upon dissolution of small ions. In analogy to the previously discussed AlCl$_3$ mixtures with imidazolium- and pyridinium-based ionic liquids (see section 4.1), in which speciation of aluminum as [AlCl$_4$]$^-$ or [AlCl$_3$]$^-$ was inferred by IR and Raman spectroscopies,$^{390}$ spectrometric studies have been carried out for other metals, for instance, tantalum and niobium, whose deposition process cannot be done in water.$^{390,391}$ Babushkina na$^{390}$ studied TaCl$_5$-[Py$_1$$_4$]Cl mixtures using IR spectroscopy$^{391}$ over a wide range of compositions at room temperature. It has been found that all of the vibrational modes of [Py$_1$$_4$]$^+$ are

Figure 44. Comparison of Raman (top) and IR (bottom) spectra of [C$_4$C$_1$im][CH$_3$COO] and its mixtures with CO$_2$ (red) and 13CO$_2$ (blue) (mole fraction less than ca. 0.3). The arrows pinpoint the three new bands assigned to 1-butyl-3-methylimidazolium-2-carboxylate. Reproduced with permission from ref 162. Copyright 2012 American Chemical Society.
disturbed upon dissolution of the tantalum salt, the ring-breathing vibrations within 890–930 cm⁻¹ being the most affected modes exhibiting change on relative intensities and frequency shift depending on the TaCl₅ concentration.

Using Raman spectroscopy, Alves et al. studied NbCl₆⁻, [C₄C₁im][Cl] and ZnCl₂-[C₄C₁im][Cl] over a wide range of compositions at room temperature. Besides speciation of niobium (NbCl₆), NbCl₉ and ZnCl₂, and ZnCl₈, these authors reported several changes in the Raman spectra of the mixtures in comparison with the neat ionic liquid spectrum, in particular, in the C–H modes of the imidazolium. It has also been found by Goujon et al. in water-ZnCl₂ or water-MgCl₂ mixtures with [C₄C₁im][Cl]. Andriyko et al. studied TiF₄-[C₄C₁im][BF₄] using IR spectroscopy over a wide range of concentrations. The authors were able to observe spectral features, indicating the formation of [TiF₆]³⁻ and a heteronuclear complex between TiF₄ and the anion, [TiBF₄]⁻. They also found decreasing intensity of anion bands because of a side reaction leading to BF₄⁻ evolution and formation of [TiF₆]³⁻.

Arellano et al. studied Zn[NTf₂]₂-[C₄C₁im][NTf₂] mixtures using IR spectroscopy with the support of quantum chemical calculations. These authors claim that a new anionic species, [Zn(NTf₂)₃]⁻, is formed upon the addition of a stoichiometric amount of the solute. Formation of [Zn(NTf₂)₃]⁻ results in frequency shift of [NTf₂]⁻. In [C₄C₁im][NTf₂], of the imidazolium modes, in particular the ν(C–H) mode. Curve-fit spectra showed significant changes, such as the number of components in the spectral range of 700–820 cm⁻¹, between spectra of mixture and the neat ionic liquid, but the authors did not address this issue.

In line with the zinc coordination compound, there are similar reports of stable compounds formed between ytterbium and europium with [NTf₂]⁻.

Liu et al. studied 0.2 mol L⁻¹ solutions of Zn[CF₃SO₃] in [C₄C₁im][CF₃SO₃], [C₄C₁im][CF₃SO₄], and [C₄C₁im][CF₃SO₃]. At 393 K, using Raman spectroscopy, the authors considered the δ₁(C≡N) in order to infer about the coordination of Zn²⁺ ions and the changes on local environment upon addition of the solute. The authors found that addition of Zn²⁺ causes a higher wavenumber shoulder in the δ₁(C≡N) Raman band due to those anions coordinating the Zn²⁺, while the lower wavenumber band is assigned to uncoordinated (“free”) anions. Methylolation of the imidazolium ring (i.e., from [C₄C₁im]⁺ to [C₄C₁C₁im]⁺), implies larger splitting of vibrational frequencies between free and bounded anions. The authors estimated the coordination number of anions around Zn²⁺ from the ratio between the band areas of free and bounded anions. In the case of the liquid based on [C₄C₁im][C₂C₁im] and [C₂C₁im][C₂C₁im], the most favored species are [Zn(CF₃SO₃)₃]⁻, [Zn(CF₃SO₄)₄]⁻, and [Zn(CF₃SO₃)₅]⁻, respectively.

Oliveira et al. using Raman spectroscopy studied the dissolution of [NH₄]⁺, with [CH₃COO]⁻, Cl⁻, SCN⁻, and [C₂SO₄]⁻ as counterions, and Na⁺, with [CH₃COO]⁻ and SCN⁻ as counterions, in [C₄C₁im][CH₃COO]. The authors showed that the [CH₃COO]⁻ mode at 910 cm⁻¹ is a good probe of the local environment as the corresponding Raman band is sensitive to the dissolved species. Chimdi et al. studied Na[N(CN)₂]-[Pyr₄]⁺[N(CN)₂] mixtures using Raman spectroscopy, whereas Carstens et al. studied Na[N(SO₂F₂)₂]-[Pyr₄]⁺[N(SO₂F₂)₂] and Forsyth et al. studied Na[NTf₂]-[Pyr₄]⁺[NTf₂] mixtures using Raman and ATR spectroscopies. Chimdi et al. and Carstens et al. reported only frequency and intensity changes of Raman bands related to anion modes, but Forsyth et al. observed also the occurrence of shoulders at 534, 576, 598, 651, and 1150 cm⁻¹ in IR bands, the latter being assigned to the twisting mode of the pyrrolidinium ring.

Lithium cation solutions in ionic liquids have been widely studied because of the application as electrolyte in lithium batteries. Ionic liquids based on the [NTf₂]⁻ anion show remarkable structural and dynamical changes when mixed with the lithium salt. For example, it was shown by NMR measurements that in Li[NTf₂]-[C₂C₁im][NTf₂] the Li⁺ self-diffusion coefficient drops by almost a third when the concentration ranges from 2% to 22% of Li⁺. Nicolau et al. using OKE spectroscopy estimated that the viscosity of [C₂C₁im][NTf₂] increases by almost ten times when approximately 40% mole fraction of Li⁺ is added. The overall trend for different systems which have been studied is that increasing Li⁺ content results in increase of viscosity and density and decrease of self-diffusion coefficient and conductivity. These effects on transport coefficients upon addition of Li⁺ are accompanied by conformational changes of the [NTf₂]⁻ anion as revealed by vibrational spectroscopy.

Lassègues et al. and Dulong et al. used Raman spectroscopy to study mixtures of [C₂C₁im][NTf₂] and [C₂C₁im][NTf₂] with Li[NTf₂] over a wide range of composition. The authors deconvoluted the anion Raman band with the maximum at ~745 cm⁻¹ into two components, the lower wavenumber component being assigned to uncoordinated (“free”) [NTf₂]⁻ and the higher wavenumber component to coordinated (“bounded”) [NTf₂]⁻ to Li⁺. These authors evaluated the coordination number of Li⁺ equal to two and then inferring for the formation of [Li(NTf₂)₂]⁻ species in line with the proposition of Umebayashi et al. and Müllner et al. such complexes are weakly bonded, being promptly destabilized in the presence of other highly coordinating solvents (e.g., diglyme, tetraglyme, and ethylene carbonate). As pointed out by Martins et al., the formation of [Li(NTf₂)₂]⁻ is also influenced by water content. The splitting of the 745 cm⁻¹ band depends on the Li⁺ molar fraction, and a pseudoisosbestic point is observed in the Raman spectrum. Furthermore, Umebayashi et al. showed that in the series of alkali cations, from Li⁺ to Cs⁺, the coordination number grows from two to four. Monteiro et al. argued that the formation of [Li(NTf₂)₂]⁻ is the main reason for the decrease of Li⁺ ionic mobility and conductivity in Li[NTf₂].

Duluard et al. studying [C₂C₁im][NTf₂] mixtures with Li⁺ pointed out that the conformation of the butyl chain remains essentially uncharged upon dissolution of Li⁺. Umebayashi et al. and Lassègues et al. addressed the issue of [NTf₂]⁻ conformation around the Li⁺ ion, analyzing the fingerprint range of the Raman spectrum of the [NTf₂]⁻ anion with the aid of quantum chemistry calculations at the DFT/B3LYP level of theory. In both of these papers, the authors concluded that 4033 cisdion conformation is favored in the 1:1 (Li⁺: [NTf₂]⁻) complex, in contrast to the situation in the neat ionic liquid, in which the transoid conformation dominates. In the case of 1:2 complex, the authors suggest that the complex structures involves the two anions in cisoid or transoid, or a mix of cisoid–transoid conformations. Lassègues et al. claim that the mix of [NTf₂]⁻ conformers gives better agreement to the fingerprint region of the Raman spectra.
The above-mentioned effects of Li⁺ dissolution on the Raman spectrum of [C₄C₁im][NTf₂] is illustrated in Figure 45.

Figure 45. Comparison between Raman spectra of pure [C₄C₁im][NTf₂] (red line), solid Li[NTf₂] (black line), and the mixture Li[NTf₂] = [C₄C₁im][NTf₂] at molar fraction of Li[NTf₂] equal to 0.37 (blue line). Spectra have been normalized by the most intense band at each spectral window.

This figure shows Raman spectra of pure [C₄C₁im][NTf₂], solid Li[NTf₂], and the mixture, in the range of 250–450 cm⁻¹, which characterizes the [NTf₂]⁻ conformation and the 741 cm⁻¹ band, whose frequency shift and split characterizes coordinated and uncoordinated [NTf₂]⁻. Despite identifying more than one possible arrangement for the [Li(NTf₂)₂]⁻ complex, no more than two components were assumed under the band at ~745 cm⁻¹. In contrast, Pitawala et al. considered three bands in the fit of the 741 cm⁻¹ Raman band in Li[NTf₂] = [Pyr₁$_n$] in [NTf₂] mixtures and reached the same coordination number as previous works for high molar fractions of Li⁺. However, for low concentrations of Li⁺ (equal or below 0.05), the authors obtained a coordination number as high as four. Change in coordination number might have consequences in transport coefficients, glass transition, and melting temperatures of the mixtures.

It is worth stressing that only part of the literature concerning ionic liquid solutions was reviewed in this section proper to the broadness of the theme and the large number of examples in which vibrational spectroscopy served only as a complementary tool to better understand some process (e.g., cellulose and carbohydrates dissolution) or for the characterization of new materials. It is also worth mentioning solvate ion liquid solutions, which are systems composed from weakly coordinating anions such as [NTf₂]⁻, small cations (e.g., Li⁺) and a chelating molecular solvent such as tetraglyme, not discussed in this review. Such systems are of increasing interest as their properties might extend the range of applications of ionic liquids.

8. CONCLUDING REMARKS

In this review, we discussed the application of vibrational spectroscopy for getting information on structure and intermolecular interactions in ionic liquids and the related experimental and theoretical issues. Quantum chemistry calculations of vibrational frequencies beyond the harmonic approximation may be needed for proper assignment and for including important anharmonicity effects on vibrational spectra of ionic liquids (e.g., Fermi resonance). Strong ionic interactions may imply that an ab initio calculation of vibrational frequencies for an isolated ion eventually only estimates the frequencies when compared with the actual spectra of the liquid phase. Fortunately, the computational resources available today allow for quantum chemistry calculations of vibrational frequencies for clusters made of a few ion pairs. However, the approach of cluster calculation still relies on an optimized geometry of minimum energy. Thus, ab initio molecular dynamics simulations of ionic liquids open the perspective for vibrational frequency calculations with the proper account of liquid dynamics. On the experimental point of view, linear IR and Raman spectroscopies of ionic liquids, which were the focus of this review, are being recently extended for time-resolved vibrational spectroscopy. Structural fluctuations of the local environment experienced by a probe oscillator cause vibrational dephasing due to energy relaxation and loss of phase (pure dephasing). The traditional approach using linear IR and Raman spectroscopies by Fourier transforming the band shape in order to get time correlation functions of vibrational dephasing and reorientational dynamics has been applied for the CN stretching mode of ionic liquids containing cyano-anions since the corresponding Raman band is relatively free of overlapping bands. However, this methodology is not fully appropriate when processes of multiple time ranges simultaneously contribute with homogeneous and inhomogeneous mechanisms for the band shape. Thus, perspectives for vibrational spectroscopy of ionic liquids include ongoing studies by time-resolved techniques, such as time-resolved IR and Raman spectroscopy and coherent anti-Stokes Raman scattering (CARS) providing insights on the short-time molecular dynamics. For instance, time-resolved CARS measurements give dephasing times in the subpicosecond range for C–H stretching modes of 1-alkyl-3-methylimidazolium cations that can be related to flexibility of molecular structure and the strength of different sites for hydrogen bonding to the anion. Time-resolved IR spectroscopy has also been used to follow the time evolution of modes belonging to molecule probes dissolved in ionic liquids. This allows addressing the molecular dynamics at the different time scales of fluctuations of the hydrogen bond structure and reorientational motions and the relative contributions of homogeneous and inhomogeneous broadening to the band shape. Thus, time-resolved vibrational spectroscopy is expected to provide experimental data related to short-time molecular dynamics allowing for direct comparison to results of computer simulations of ionic liquids. Nevertheless, there is plenty of room for applications of linear IR and Raman spectroscopies in many areas related to the ones discussed in this review. Besides the application on ionic liquid solutions discussed in this review, vibrational spectroscopy is a complementary technique within the broad field of research on hybrid materials. Vibrational spectroscopy has been used in combination with other techniques to characterize ionic liquid interactions with nanotube and graphene, clay, polyelectrolytes, carboxydrates, etc. Furthermore, surface-enhanced Raman scattering (SERS) studies have been reported for ionic liquids with different metals as substrates. Within the context of studies on phase transitions, vibrational spectra of ionic liquids have been reported as a function of temperature, at atmospheric pressure, or as a function of pressure, at room temperature.
Simultaneous variation of temperature and pressure aiming more complete mapping of the phase diagrams most probably will be the subject of further vibrational spectroscopy studies of ionic liquids.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemrev.6b00461.

IR and Raman spectra recorded in this work are available as TXT files. Each file is identified by the number of the figure, the ionic liquid name, and whether it corresponds to Raman or IR spectrum. The files give Raman and IR spectra covering the same spectral window as shown in the corresponding figure of the paper. The file DAC_Crystallization.wvm is a movie showing the real time crystallization process of [C$_n$C$_2$im][NtF$_2$] inside the diamond anvil cell at 0.7 GPa and room temperature (ZIP).

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#### Notes

The authors declare no competing financial interest.

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Luiz Felipe de Oliveira Faria received his degree in chemistry from Federal University of Juiz de Fora in 2010 and his Ph.D. degree from University of São Paulo (Brazil) in 2015. He completed his Ph.D. under the supervision of Prof. Dr. Mauro C. C. Ribeiro on the structure and phase transitions of ionic liquids in different conditions of temperature and pressure. He is currently a postdoc in Prof. Mauro C. C. Ribeiro group, and his research has been focused on the structure and phase transitions of ionic liquids under high pressure using Raman spectroscopy and X-ray scattering techniques.

Mauro Carlos Costa Ribeiro is an Associate Professor at the Chemistry Institute of the Universidade de São Paulo, IQ-USP. Mauro obtained his Bachelor degree in Chemistry in 1989 from Universidade Santa Cecilia (Santos-SP). He obtained his Master’s degree in 1992 and his Ph.D. degree in 1995, both from Universidade de São Paulo under supervision of Prof. Paulo S. Santos. His Master’s studies concerned calculations of resonant Raman spectra and his Ph.D. thesis on Raman spectroscopy and molecular dynamics of liquids. He started teaching at IQ-USP in 1996. Mauro spent one and a half years (1996–1998) as a postdoc in the group of Prof. Paul A. Madden at Oxford University, U.K., working with molecular dynamics of high-temperature molten salts. After returning to São Paulo, he started working with vibrational spectroscopy and molecular dynamics simulation of room-temperature ionic liquids. He also spent shorter periods working in the groups of Prof. Giancarlo Ruocco in 2007 (Università di Roma La Sapienza) and Prof. Agliao A. H. Pieda in 2013 (Université Blaise Pascal, Clermont-Ferrand, France). His research concerns structure and dynamics of ionic liquids with particular focus on changes observed along the glass transition and crystallization taking place under low temperature or high pressure.

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