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New Interpretation of the CH Stretching Vibrations in Imidazolium-Based Ionic Liquids

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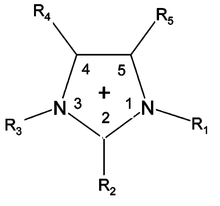
In ionic liquids composed of alkyl-substituted imidazolium cations and weakly coordinating anions such as bis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2N^-$, the stretching vibrations of the imidazolium CH groups are shown to interact by Fermi resonance with the overtones and the combination of two in-plane ring vibrations. This new assignment, based on isotopic substitutions and anharmonic frequency calculations for gas phase cations, implies that these imidazolium cations do not establish any strong and directional C−H···anion hydrogen bond.

In recent years, much work has been devoted to the understanding of the nanostructural organization in ionic liquids (ILs).[1,2] In particular, the role played by hydrogen bond interactions in controlling the structure and properties has been widely discussed.[3−15] Typically, infrared (IR) spectra have been interpreted in terms of CH···anion interactions established by the often imidazolium-based cations, in particular via the $C_{(2)}$-H bond. However, in spite of a general agreement that the imidazolium CH oscillators constitute excellent spectroscopic probes for hydrogen bonding, different assignments of their stretching vibrations, νCH, can be found in the literature.[8−15] In the present work, we propose a completely new and unified assignment which takes into account the anharmonic character of the νCH vibrations and of their interactions with overtones and combination of two in-plane ring modes situated in the 1500−1600 cm^{-1} region. With weakly coordinating anions, such as bis(trifluoromethanesulfonyl)imide anion ($TFSI^-$), there is no need to consider any directional hydrogen bonds. Anharmonic ab initio calculations (B3LYP/6-31G**) of the IR spectra have been performed for various isolated cations described in Scheme 1, including H/D isotopic derivatives.[16] The details of the calculations, sample origins, preparation of the isotopic derivatives and recording of the IR spectra will be given in a more extended paper.

Let us first recall that the three νCH vibrations of an imidazolium ring, Im^+ (C_{2v} symmetry), are usually described in terms of in-phase and out-of-phase stretching vibrations of the H-$C_{(4)}$-$C_{(5)}$-H group, noted $\nu_{ip}C_{(4,5)}H$ and $\nu_{op}C_{(4,5)}H$, respectively, and of the stretching vibration of the $C_{(2)}H$ bond, noted $\nu C_{(2)}H$. IR and Raman studies of aqueous solutions of imidazolium chloride have shown that the $\nu_{ip}C_{(4,5)}H$ (A_1), $\nu C_{(2)}H$ (A_1), and $\nu_{op}C_{(4,5)}H$ (B_2) vibrations of the imidazolium cation solvated by water molecules are situated at 3180, 3153, and 3147 cm^{-1}, respectively.[17] The three in-plane bending modes, δCH, occur in the 1300−1050 cm^{-1} region and the three out-of-plane bending modes, γCH, in the 900−750 cm^{-1} region. The imidazolium cation is also characterized by nine ring vibrations that can easily couple with one of the δCH or γCH modes having the same symmetry.[17] The in-plane R_1 (A_1) and R_2 (B_2) modes are situated at 1587 and 1535 cm^{-1}, respectively.[17] Substitution of the two N-H protons of Im^+ by two methyl groups gives the MMI^+ cation, still of C_{2v} symmetry, as the two methyl groups are nearly free rotors. Asymmetric alkyl substitution, as in the EMI^+, BMI^+, and $BMMI^+$ cations (see Scheme 1), lowers the local symmetry of the imidazolium ring and introduces conformational isomerism.[18−20] However, the characteristic vibrations of the imidazolium ring in all these systems change only smoothly with the symmetry lowering, as illustrated in Figure 1. The first three ILs present two main absorptions, although with internal structure, at 3160 ± 15 and 3120 ± 15 cm^{-1}. As the latter is absent in BMMI-TFSI, it has been assigned to the $\nu C_{(2)}H$ vibration, while the first absorption band at ~3160 cm^{-1} has been assigned to the $\nu_{ip}C_{(4,5)}H$ and $\nu_{op}C_{(4,5)}H$ vibrations. Thus, the $C_{(2)}$-H bond would establish stronger hydrogen bonds than the other two CH bonds, in agreement with its stronger acidity and, in addition, as the red-shift of $\nu C_{(2)}H$ by about 40 cm^{-1} has not been reproduced by any calculation for an isolated cation, a natural extension was to develop various models of hydrogen-bonded clusters. As an example, the two components of the second absorption in EMI-TFSI at ~3125 and ~3105 cm^{-1} were attributed to distinct $\nu C_{(2)}H$ vibrations in two families of hydrogen-bonded species.[8−10]

SCHEME 1: Nomenclature Used for the Investigated Alkyl-Substituted Imidazolium Derivatives



Imidazolium R_1-R_5 = H	Im^+
1,3-dimethyl imidazolium	MMI^+
1-ethyl-3-methyl imidazolium	EMI^+-d_0
1-ethyl-2d_1-3-methyl imidazolium	EMI^+-d_1
1-ethyl-3-methyl-4,5-d_2- imidazolium	EMI^+-d_2
1-ethyl-3-methyl-2,4,5-d_3- imidazolium	EMI^+-d_3
1-butyl-3-methyl imidazolium	BMI^+
1-butyl-2,3-dimethyl imidazolium	$BMMI^+$

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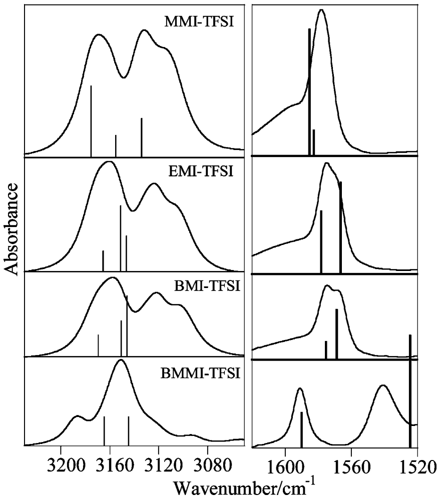

Figure 1. IR spectra at room temperature of the four indicated ILs in the region of the imidazolium CH stretching vibrations (left) and R_1, R_2 ring vibrations (right). The calculated anharmonic wavenumbers (solid vertical lines) are multiplied by a scaling factor of 0.9906 in the νCH region, but unchanged for the in-plane ring modes. Only the more abundant conformers are represented (nonplanar for EMI^+, GA for the butyl chains of BMI^+ and $BMMI^+$). The intensities are from the harmonic approximation.

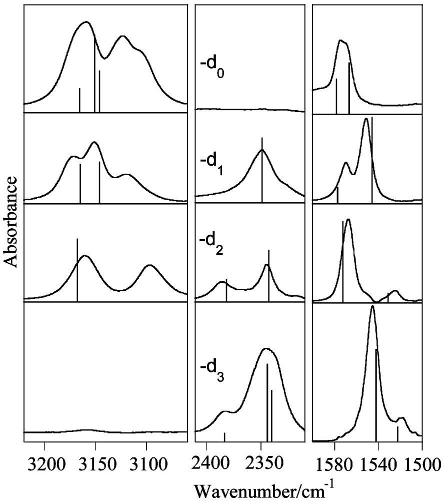

Figure 2. Same as Figure 1 for the four indicated isotopic derivatives of EMI-TFSI in the region of the imidazolium CH stretching vibrations (left), CD stretching vibrations (middle), and R_1/R_2 ring vibrations (right). The calculated νCH and νCD wavenumbers are multiplied by 0.9906.

For a better understanding of the νCH imidazolium vibrations, we here apply the classical method of H/D isotopic substitution. The EMI-d_1 derivative exhibits a unique $\nu C_{(2)}D$ band at 2350 cm^{-1} while the two distinct bands observed in the νCH region at 3173 and 3151 cm^{-1} can be assigned to the $\nu_{ip}C_{(4,5)}H$ and $\nu_{op}C_{(4,5)}H$ vibrations, respectively (Figure 2). However, there is an additional unexplained band at 3119 cm^{-1} that does not vanish even at high deuteration rates. In the EMI-d_2 derivative, two bands are observed at 3160 and 3096 cm^{-1}. Both of them can hardly be assigned to $\nu C_{(2)}H$ vibrations because $\nu C_{(2)}D$ gives a simple band in EMI-d_1. Even more problematic is the νCD absorption profile of the EMI-d_3 derivative. It is quite different from the νCH profile in EMI-d_0, while being in good agreement with the calculated one. Finally, it appears that, under the hypothesis of an isolated cation, all the observed νCD, R_1 and R_2 vibrations, and most vibrations at lower wavenumbers (not shown) are reproduced by the anharmonic frequency calculation, but not all the bands observed in the νCH region can be reproduced (Table SI1). Therefore, we postulated that the νCH region might be complicated by the presence of overtone and combination bands. A close examination of the results of the anharmonic calculations do confirm the existence of strong coupling constants between, on one hand, the νCH modes and, on the other hand, the R_1 and R_2 ring modes, their overtones $2R_1$ and $2R_2$, and the combination $R_1 + R_2$ (Table SI2). Hereby, a completely new kind of assignment can be envisaged (Table SI1): in brief, the $\nu_{ip}C_{(4,5)}H$, $\nu C_{(2)}H$, and $\nu_{op}C_{(4,5)}H$ modes are all contained in the first absorption at ~3160 cm^{-1} in the MMI-TFSI, EMI-TFSI, and BMI-TFSI ILs (Figure 1), whereas the structure of the 3120 cm^{-1} absorption is produced by Fermi resonances with the overtones and the combination of R_1 and R_2. In BMMI-TFSI, the appearance is quite different, not only because the $\nu C_{(2)}H$ mode has been substituted away, but also because the overtone of the R_1 mode situated at 1591 cm^{-1} is hidden within the 3151 cm^{-1} main band, while the overtone of the R_2 mode situated at 1541 cm^{-1} falls below 3080 cm^{-1}. The weak band at 3090 cm^{-1} can be explained by the $R_1 + R_2$ combination in Fermi resonance with $\nu_{op}C_{(4,5)}H$ (Table SI2). Similarly, in the EMI-d_1 derivative (Figure 2), the 3120 cm^{-1} band corresponds to $2R_1$ and $R_1 + R_2$ in Fermi resonance with $\nu_{ip}C_{(4,5)}H$ and $\nu_{op}C_{(4,5)}H$, respectively, whereas the overtone of R_2, situated at 1551 cm^{-1}, falls below 3100 cm^{-1}. In EMI-d_2, the $\nu C_{(2)}H$ mode at 3160 cm^{-1} interacts with the $2R_1$ overtone at 3096 cm^{-1}. The advantage of the anharmonic calculation is not only to achieve a better agreement between the calculated and observed wavenumbers, but also to reveal the involved cubic force constants.[21,22]

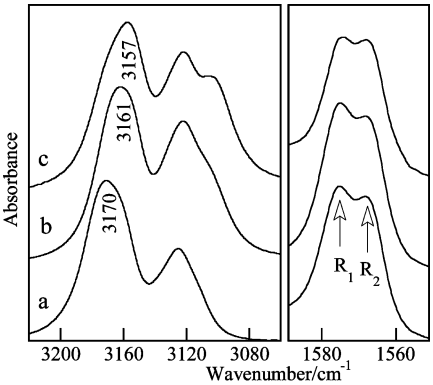

Figure 3. IR spectra of BMI-PF_6 (a), BMI-BF_4 (b), and BMI-TFSI (c) in the region of the imidazolium CH stretching vibrations (left) and R_1/R_2 ring vibrations (right).

Finally, there is now no need to invoke hydrogen bond interactions to interpret the νCH and νCD IR spectra of imidazolium and TFSI-based ILs. Our assignment applies also to the Raman spectra and to other weakly coordinating anions such as $AlCl_4^-$,[3] BF_4^-,[11] or PF_6^-. This is a surprising conclusion as far as vibrational spectroscopy is concerned, but some authors have already claimed that C−H···anion hydrogen bonds are not essential in the attraction of ion pairs.[1,2,12,14] Nevertheless, the imidazolium CH oscillators remain sensitive to the nature of the anion, that is, to a kind of global solvent effect. Let us recall that the dielectric constant, although its use for ILs is still debated, varies for example from 15.2 for EMI-TFSI to 12.8 for EMI-BF_4.[23] As shown in Figure 3, the mean position of the νCH band moves from ~3157 cm^{-1} with TFSI$^-$, to ~3161 cm^{-1} with BF_4^- and ~3170 cm^{-1} with PF_6^-; at the same time, the R_1 and R_2 vibrations are practically unchanged. It is interesting to note that a shift of νCH to higher/lower wavenumbers decreases/increases the interaction with the overtones and combination of the R_1 and R_2 vibrations. Therefore, the changes occurring in the relative intensities at ~3160 and ~3120 cm^{-1} are not governed by a classical equilibrium between associated and dissociated hydrogen bonded species but result from a modulation of the interaction between the νCH vibrations and the R_1 and R_2 overtones and combination. We believe that this new assignment can help understanding the temperature, pressure, and dilution effects on imidazolium-based ILs.

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Supporting Information Available: Experimental and calculated IR wavenumbers of the CH imidazolium stretching vibrations, R_1 and R_2 in-plane ring modes, $2R_1$ and $2R_2$ overtones and $R_1 + R_2$ combination in various alkyl-imidazolium-TFSI ILs at room temperature (Table SI1). Calculated quartic and cubic coupling constants between the imidazolium CH stretching vibrations and the R_1 and R_2 ring modes (Table SI2). This material is available free of charge via the Internet at http://pubs.acs.org.

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