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Hydrogen bonding in ionic liquids probed by linear and nonlinear vibrational spectroscopy

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Abstract. Three imidazolium-based ionic liquids of the type $[C_n mim][NTf_2]$ with different alkyl chain lengths (n = 1, 2 and 8) at the first position of the imidazolium ring were studied applying infrared, linear Raman and multiplex coherent anti-Stokes Raman scattering spectroscopy. The focus has been on the CH-stretching region of the imidazolium ring, which is supposed to carry information about a possible hydrogen bonding network in the ionic liquid. The measurements are compared with calculations of the corresponding anharmonic vibrational spectra for a cluster of $[C_2 mim][NTf_2]$ consisting of four ion pairs. The results support the hypothesis of weak hydrogen bonding involving the C(4)–H and C(5)–H groups and somewhat stronger hydrogen bonds of the C(2)–H groups.

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1. Introduction

Ionic liquids (ILs) have unique and fascinating properties that provide a remarkable opportunity for their application to modern science and technology [1–7]. These liquid materials offer a wide range of possible applications, for example, as solvents for reaction and material processing, as extraction media or as the working fluid in mechanical processes. The physical properties and solvent behavior of ILs are the key features for any application. The structure and properties of these Coulomb systems are mainly determined by the type and strength of the intermolecular interactions between anions and cations. In particular, the subtle balance between Coulomb forces, hydrogen bonds (HBs) and dispersion forces is of great importance for understanding ILs. It is assumed that, in particular, hydrogen bonding has an important role in the properties and reaction dynamics of these Coulomb systems [8-11]. Strong evidence for the existence of hydrogen bonding is provided by x-ray diffraction, mid-infrared (IR) and NMR spectroscopy. The observed indications of hydrogen bonding in imidazolium-based ILs are shorter C-H anion distances, red shifted C-H stretching frequencies and downfield shifted C-H proton chemical shifts [12–22]. However, it has been argued that the corresponding signatures in the IR spectra can also result from other contributions and that hydrogen bonding is not essential for understanding the properties of ILs [23–27]. The strength and properties of the anion–cation interaction including hydrogen bonding have also been studied by theoretical methods [28-31].

In particular, the C–H stretching vibrations in imidazolium-based ILs should give some information about the existence and strength of hydrogen bonding in this Coulomb system. So far, the interpretation of the C–H region is highly controversial [32, 33]. Exemplarily, let us consider ILs of the type [1-alkyl-3-methyl imidazolium][bis(trifluoromethanesulfonyl)imide] (see scheme 1) with the acronyms [C_nmim][NTf₂], where n = 1, 2 or 8 denotes the length of the alkyl chain at the first position of the imidazolium ring.

Their IR spectra of the C–H stretching region show contributions between 2800 and 3000 cm^{-1} , which can be clearly referred to as the CH₂ and CH₃ stretching vibrations of the

2



Scheme 1. Nomenclature used for [1-alkyl-3-methyl imidazolium][NTf₂] ILs investigated in this work.



Scheme 2. Interpretation of the frequency region of C–H stretching vibrations in imidazolium-based ILs as suggested by Grondin *et al* [32].

alkyl groups at the nitrogen atoms of the imidazolium ring. For the adjacent frequency range between 3100 and 3200 cm⁻¹, two main interpretations are given (scheme 2). Grondin *et al* [32] claim that the high-frequency contributions at 3160 ± 15 cm⁻¹ can be assigned exclusively to all C-H stretching vibrations of the imidazolium cation (C(2)-H, C(4)-H and C(5)-H), whereas the absorption at 3120 ± 15 cm⁻¹ results, as indicated in scheme 2, from overtones $(2R_1, 2R_2)$ and combination tones $(R_1 + R_2)$ of two in-plane ring vibrations R_1 and R_2 which form Fermi resonances with the C-H stretching vibrations. Albeit that Fermi resonances of such combination and overtone transitions might contribute in the region at $3120 \,\mathrm{cm}^{-1}$, Ludwig *et al* claim that only a single vibrational band at 3160 cm^{-1} cannot account for the three C(2)–H, C(4)-H and C(5)-H stretches [33]. They suggest that the band can be assigned to the C(4)-H and C(5)–H stretches, whereas the C(2)–H vibrational mode is shifted by about 50 cm^{-1} to lower frequencies due to its stronger acidic character and thus falls into the frequency range of the overtones and combination tones. A red-shift of the C(2)-H stretching frequency relative to those of C(4)–H and C(5)–H is in accordance with a stronger NMR downfield proton chemical shift of about 1 ppm for C(2)-H compared to C(4,5)-H [21]. A further indication of this notion has already been observed by Grondin et al [32]. In isotopic substitution experiments, they could record the C(2)–D, C(4)–D and C(5)–D stretching vibrational modes in the frequency range between 2250 and $2400 \,\mathrm{cm}^{-1}$. The advantage of these experiments is that this frequency range is not overcrowded by overtones and combination tones of the imidazolium ring. Grondin et al observed the C(2)–D vibrational band at 2350–2355 cm⁻¹ and the C(4,5)–D vibrational

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bands at 2388–2393 cm⁻¹. Thus, the C(2)–D frequencies are clearly red-shifted by 38 cm⁻¹. Following the equation of the simple harmonic oscillator and taking into account the difference in reduced masses (Grondin *et al* estimated an isotopic ratio of 1.33), a frequency shift of $\Delta \nu = 50.5$ cm⁻¹ for the vibrational bands of C–H bonds is expected, in agreement with the suggestions of Ludwig *et al* [27, 33].

To conclude, in the frequency range between 3100 and 3200 cm⁻¹, Fermi resonances of C–H stretching modes with combinations and overtones of ring vibrations seem to cause complicated vibrational signatures and prohibit a straightforward assignment. To clarify the situation and to obtain a reliable assignment we record the spectra of ILs with different alkyl chains in this frequency range by a variety of spectroscopic methods and compare the results with anharmonic calculations of the vibrational frequencies. Besides linear Fourier transform (FT) IR and FT-Raman spectroscopy, we also apply multiplex coherent anti-Stokes Raman scattering (CARS) spectroscopy using ultrashort laser pulses, which gives a different contrast owing to its nonlinear character and its sensitivity to vibrational bands in the C–H stretching region and a molecular understanding of the interactions in these Coulomb systems are achieved.

2. Experimental techniques

2.1. The preparation and handling of ionic liquids

The studied ILs, which include the same anion bis(trifluoromethylsulfonyl)imide (NTf₂⁻) but various cations, i.e. 1,3-dimethyl imidazolium, 1-ethyl-3-methyl imidazolium and 1-octyl-3-methyl imidazolium, were of commercial origin (Iolitec GmbH, Denzlingen, Germany) with a stated purity of >98%. All substances were additionally dried in vacuum ($p = 8 \times 10^{-3}$ mbar) for approximately 24 h. The water content was then determined by Karl–Fischer titration and was less than 200 ppm in all cases. Further purification was not carried out.

2.2. Infrared measurements

Fourier transform infrared (FTIR) measurements were carried out with a Bruker Vertex 70 FTIR spectrometer. The equipment for the IR measurements consists of a potassium bromide beam splitter and a room temperature DLATGS (deuterated L-alanine doped triglycene sulfate) detector with preamplifier. The accessible spectral region for this configuration lies between 1000 and 4500 cm⁻¹. An LOT-Oriel variable-temperature cell equipped with calcium fluoride (CaF₂) windows having a path length of 0.012 mm was used for the IR measurements in transmission. For each spectrum 100 scans were recorded at a spectral resolution of 1 cm⁻¹.

2.3. Linear Raman measurements

The Bruker Vertex 70 FTIR spectrometer is equipped with an extension for Raman measurements, the RAM II FT-Raman module. For the linear Raman measurements an Nd:YAG laser (1064 nm) with a power of 1 W from Klastech was used. The signal was detected at a nitrogen-cooled highly sensitive germanium diode detector. This RAM II configuration provides a spectral range of $50-4000 \text{ cm}^{-1}$ and 400 scans were taken at a resolution of 1 cm^{-1} . For a reliable comparison, all spectra were recorded at 298 K.

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Figure 1. Cluster model of $[C_2mim][NTf_2]$ (geometry at a stationary point at the B3LYP/6-31+G(d) level of theory). The three HBs are marked whose IR spectral signatures are in the focus of the anharmonic vibrational model.

2.4. Coherent anti-Stokes Raman scattering

In addition to linear Raman measurements, time-resolved multiplex CARS with ultrashort excitation and narrowband probing is applied. This technique provides higher spectral contrast compared to linear Raman and allows for the characterization of dephasing kinetics of molecular vibrations [35, 36]. The CARS setup is described in detail in [37]. It is based on a femtosecond noncollinear optical parametric amplifier (NOPA) generating sub-50 fs Stokes pulses and a modified picosecond NOPA providing Raman pump and probe pulses with a bandwidth of about $20 \,\mathrm{cm}^{-1}$. The broadband Stokes pulses have a central wavelength of 604 nm and the pump and probe pulses are tuned to 510 nm. The pulse energies are a few hundreds of nJ. The three beams are arranged in a folded BOXCARS geometry for phase matching and focused onto the sample to a common spot with a diameter of about $100 \,\mu$ m. The Stokes and the pump pulses excite vibrational coherences of Raman active modes in the CH-stretching region. The interaction of the vibrational coherences with the probe pulses results in a nonlinear polarization and the laserlike CARS signal. The signal is coupled into a spectrograph by a glass fiber and recorded by an array detector. The Raman probe can be time delayed with respect to the Stokes and pump pulses to reduce the non-resonant background and to measure the decoherence time of the vibrational excitation.

3. Theoretical model

Anharmonic vibrational spectra have been calculated for a cluster model comprising four ion pairs ($[C_2mim][NTf_2]$) in gas phase. As shown in figure 1 this cluster supports a motif where all three C–H groups are hydrogen bonded to neighboring anions. In principle at least trimers



Figure 2. Normal mode displacement vectors and harmonic frequencies of those coordinates that comprise the five-dimensional model used for the interpretation of the C–H stretching region of the IR spectrum of [C₂mim][NTf₂].

are required to saturate the three potential proton donor positions at the imidazolium cation. However, in our case the bulk phase behavior (as obtained from the x-ray structures of the solid material [38]) could best be described by a tetrameric ion-pair aggregate of the [C₂mim][NTf₂]. The starting point for the generation of a potential energy surface (PES) has been the equilibrium structure as obtained from a geometry optimization at the B3LYP/6-31 + G(d) level of theory. The marked HBs are found to have the following bond lengths/angles: 2.03 Å/174°, C(2)–H...O, 2.47 Å/138°, C(4)–H...O, 2.75 Å/135°, C(5)–H...O. Note that in the common terminology these HBs would be classified as being of moderate to weak strength [39].

For the anharmonic vibrational calculation, we will use a description in terms of normal mode displacements of a set of target modes with the respective normal mode vectors spanning the PESs. Since the focus is on the C–H stretching region containing the signatures of the HBs marked in figure 1, we have chosen the corresponding three normal modes shown in figure 2 as Q_3-Q_5 . Anticipating a coupling of these modes to overtones and combination transitions of

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in-plane ring vibrations of imidazolium [27, 33], we have included the two modes Q_1 and Q_2 corresponding to modes R_1 and R_2 discussed above (cf the upper panel of figure 2) to arrive at a five-dimensional model, $\mathbf{Q} = (Q_1, \dots, Q_5)$.

Neglecting rotational effects and freezing all other normal modes of the cluster at their equilibrium positions, the Hamiltonian can be written as (using dimensionless normal mode coordinates) [40]

$$H = \sum_{i=1}^{5} \frac{\hbar\omega_i}{2} \frac{\partial^2}{\partial Q_i^2} + V(\mathbf{Q}).$$
⁽¹⁾

In general, the PES can be expressed in terms of a correlation order expansion (see, e.g., [41])

$$V(\mathbf{Q}) = \sum_{i} V^{(1)}(Q_i) + \sum_{i < j} V^{(2)}(Q_i, Q_j) + \cdots$$
 (2)

In the following, we will not aim at a quantitative comparison with experiment. After all, the cluster model cannot capture all aspects of the bulk liquid. Hence we will not only restrict ourselves to an expansion up to two-mode correlations, but also include only certain two-mode terms, i.e. those involving the interaction of the two ring deformation modes with the three C–H stretching vibrations. Thus, we use the following approximation for the two-mode PES:

$$\sum_{i < j} V^{(2)} \left(Q_i, Q_j \right) \approx \sum_{i=1}^2 \sum_{j=3}^5 V^{(2)} \left(Q_i, Q_j \right).$$
(3)

For the three vector components of the dipole moment surface (DMS), $d_{k=x,y,z}(\mathbf{Q})$, we have applied the same expansion. PES and DMS are generated on a grid comprising 14 points along the C–H stretching coordinates and 11 points for the ring deformation modes. Thus, in total, 844 single-point calculations have been performed (B3LYP/6-31 + G(d)) using Gaussian 03 [42]. Subsequently, one- and two-dimensional surfaces have been fitted by a third-order spline interpolation.

Selected eigenstates and transition dipole moments are calculated as follows. First, zeroorder states are determined according to the one-mode potentials

$$\left[\frac{\hbar\omega_i}{2}\frac{\partial^2}{\partial Q_i^2} + V^{(1)}(Q_i)\right] |\chi_{i,n_i}\rangle = E_{i,n_i} |\chi_{i,n_i}\rangle, \quad n_i = 1, \dots, N_i, \ i = 1, \dots, 5.$$
(4)

This task is accomplished by using the Fourier-grid-Hamiltonian method using 21 grid points on the fitted PES in the ranges specified in figure 6 [43]. Subsequently, this basis is used to express the two-dimensional eigenfunctions for the selected cuts of the PES, equation (3), i.e.

$$|\Psi_{\alpha}\rangle = \sum_{n_i=1}^{N_i} \sum_{n_j=1}^{N_j} C_{\alpha,n_in_j} |\chi_{i,n_i}\rangle |\chi_{j,n_j}\rangle.$$
(5)

Convergence for the transitions in the CH-stretching range could be obtained by choosing $N_i = 4$ for modes Q_1 and Q_2 and $N_i = 3$ for modes Q_3 – Q_5 . Using the resulting $N_i \times N_j$ eigenvalues and eigenfunctions the IR transition intensities shown below are defined as

$$I(\omega) = \omega \sum_{k=x,y,z} \sum_{\alpha} \left| \langle \Psi_{\alpha} | d_k(\mathbf{Q}) | \Psi_1 \rangle \right|^2 \delta(\hbar\omega - E_1 - E_{\alpha}), \qquad (6)$$

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Figure 3. FTIR spectra of $[C_n \text{mim}][\text{NTf}_2]$ imidazolium-based ILs with n = 1, 2 and 8. Left panel: the in-plane ring vibrational modes Q_1 and Q_2 are observed in the frequency range between 1550 and 1600 cm⁻¹. Right panel: the overtones and combination tones of the in-plane vibrational modes along with the CH-stretching vibrational modes are recorded in the frequency range between 3100 and 3200 cm⁻¹.

with the spectra drawn as stick spectra normalized to the maximum peak in the considered range. The transitions will be classified according the notation $(\nu_1, \nu_2, \nu_3, \nu_4, \nu_5)$, where ν_i are the number of quanta in mode Q_i .

4. Experimental results

Figure 3 shows the two spectral regions between 1500 and 1650 cm^{-1} and between 3050 and 3250 cm^{-1} of the FTIR spectra of the three investigated $[C_n \text{mim}][\text{NTf}_2]$ imidazolium-based ILs with n = 1, 2 and 8. In the first region a band around $1575 \pm 15 \text{ cm}^{-1}$ is observed which exhibits a wing extending to the blue and which seems to have a double-peak structure in the case of $[C_2 \text{mim}][\text{NTf}_2]$ and $[C_8 \text{mim}][\text{NTf}_2]$. As shown below, these features can be assigned to two in-plane vibrations Q_1 and Q_2 of the imidazolium ring.

In the second region, which covers the C–H stretching contributions of the imidazolium ring, the spectra of the three ILs exhibit two main features. The first one is at approximately $3120 \pm 15 \text{ cm}^{-1}$ and seems to consist, in all cases, of two strongly overlapping bands. The second feature appears more in the blue at approximately $3160 \pm 15 \text{ cm}^{-1}$. In the case of $[C_2 \text{mim}][\text{NTf}_2]$ and $[C_8 \text{mim}][\text{NTf}_2]$, it exhibits a shoulder in the blue wing. The assignment of these features is discussed below.

In figure 4 the Raman spectra of the three investigated ILs are presented for the two spectral regions between 1500 and 1650 cm^{-1} and between 3080 and 3250 cm^{-1} . They resemble the IR spectra, but also exhibit some interesting differences. At $1575 \pm 15 \text{ cm}^{-1}$ a band due to the inplane ring vibrations is observed and around 3120 cm^{-1} a broad feature appears which seems to consist of two bands. In all three ILs, a further band is detected at $3180 \pm 15 \text{ cm}^{-1}$, while an additional peak at $3160 \pm 15 \text{ cm}^{-1}$ can only be clearly identified in the case of $[C_2 \text{mim}][\text{NTf}_2]$ and $[C_8 \text{mim}][\text{NTf}_2]$. Care has to be taken when comparing the intensities of the Raman bands



Figure 4. FT-Raman spectra of $[C_n \text{mim}][\text{NTf}_2]$ imidazolium-based ILs with n = 1, 2 and 8. Left panel: the in-plane ring vibrational modes Q_1 and Q_2 are observed in the frequency range between 1550 and 1600 cm⁻¹. Right panel: the overtones and combination tones of the in-plane vibrational modes along with the CH-stretching vibrational modes are recorded in the frequency range between 3100 and 3200 cm⁻¹.

with the IR bands in the spectral range above 3080 cm^{-1} since the C–H stretching region of the alkyl groups is just below this frequency and exhibits strong Raman bands. The wings of these contributions may give rise to an underlying background and raise the spectral features of interest in a slope-like manner.

Figure 5(a) shows CARS spectra of $[C_2 mim][NTf_2]$ in the C–H stretching region of the imidazolium ring for different delay times between the vibrational excitation by the Raman pump and Stokes pulse and the signal generation by the Raman probe pulse. The same spectra but normalized to their maxima are depicted again in figure 5(b) for better visibility of weak features. At time zero and early delay times, broad and overlapping bands are observed. With increasing time the signal decays quickly and the spectra change their shape. The structures become more pronounced, and the bands adopt smaller widths and shift slightly to the blue. This behavior results from the interference between a nonresonant background and the resonant contributions [34, 36, 37]. The former one is due to the instantaneous electronic response of the sample and exhibits a weak frequency dependence. At a resonant contribution the difference frequency between the CARS signal and the Raman probe equals the vibrational frequency of a mode carrying Raman intensity. Since the resonant contributions are phase shifted by $\pi/2$ with respect to the nonresonant background, the vibrational signatures of the CARS spectra are strongly distorted at short delay times and the signal maxima red-shifted with respect to the Raman resonances. While the nonresonant background decreases with time according to the cross correlation between Stokes and probe pulses, the resonant contributions decay after the cross correlation with half of the vibrational decoherence time [34, 35].

At delay times above 1.3 ps, where the temporal overlap between Stokes and probe pulses is negligible, the spectral positions of the observed features fit to the bands appearing in the linear Raman spectrum although the intensity ratios are quite different and the line widths are reduced. These differences result from several effects. One reason is the different dephasing and



Figure 5. (a) CARS spectra of $[C_2mim][NTf_2]$ in the C–H stretching region of the imidazolium ring for different delay times between the CARS pump process and the probe pulse. (b) The same spectra as in panel (a) but normalized to the maximum and vertically shifted for better visibility. (c) Comparison of the CARS spectra of the three considered ILs for a delay time of 1.4 ps. The spectra are normalized with respect to their maximum and vertically shifted.

lifetimes of the distinct vibrational modes. For example, we extracted from the time-dependent CARS signal a decoherence time of 0.5 ps for the transition at $3180 \pm 15 \text{ cm}^{-1}$, whereas the other bands decay so fast that a reliable determination of the corresponding time constants is not possible. Differences between CARS and Raman spectra also result from the fact that the CARS intensity scales with the square of the Raman cross section which suppresses weak bands. In addition, the widths of bands in the CARS spectra are given by the spectral width of the probe pulse and can be smaller than the vibrational line widths [36]. This leads not only to a clearer separation of overlapping bands but also to a reduction of background signals caused by wings of strong Raman lines in the neighborhood, such as e.g. C–H stretching vibrations of alkyl groups, which seem to increase the intensity of the bands around 3120 cm⁻¹ in the linear Raman spectra.

A comparison of the CARS spectra of all three investigated imidazolium-based ILs is shown in figure 5(c) for a delay time of 1.4 ps. The band at $3180 \pm 15 \text{ cm}^{-1}$ dominates the spectra and fits nicely to the corresponding feature in the Raman spectra. For [C₂mim][NTf₂] and [C₈mim][NTf₂], a weak band is observed at slightly lower wave numbers, which is missing in the case of [C₁mim][NTf₂], confirming the observations of the Raman experiments. Further to the red, two more weak bands appear well separated in the spectra of [C₂mim][NTf₂] and [C₈mim][NTf₂]. In the case of [C₁mim][NTf₂] they are stronger, closer together and overlap, again in agreement with the Raman spectra. Overall, the comparison between linear Raman and CARS, where weak contributions and background are suppressed, is useful in identifying the relevant features.

Table 1. Harmonic and anharmonic frequencies (in cm⁻¹) as well as normalized intensities (in parentheses), calculated using diagonal anharmonicities only $(V^{(1)}(Q_i))$ as well as various cuts through two-dimensional potentials $(V^{(2)}(Q_i, Q_j))$. Note that harmonic and one-dimensional anharmonic transitions for the ring deformation modes are given after the scaling of the fundamental transition (see text). Only intensities exceeding 0.01 are reported. The experimental values are taken from the IR spectrum.

$(v_1, v_2, v_3, v_4, v_5)$	Harmonic	$V^{(1)}(Q_i)$	$V^{(2)}(Q_1, Q_3)$	$V^{(2)}(Q_1, Q_4)$	$V^{(2)}(Q_2, Q_3)$	Experiment
(0,0,0,0,1)	3311 (0.11)	3224 (0.03)	_	_	_	3173
(0,0,0,1,0)	3277 (0.37)	3189 (0.31)	_	3201 (1.00)	_	3158
(2,0,0,0,0)	3148 (0.00)	3150 (0.00)	3148 (0.05)	3138 (0.06)	_	3125
(0,2,0,0,0)	3138 (0.00)	3140 (0.00)	_	_	3141 (0.12)	3125
(0,0,1,0,0)	3216 (1.00)	3093 (1.00)	3090 (1.00)	-	3087 (1.00)	3104

5. Results and discussion

5.1. Assignment of the recorded vibrational bands

Let us first discuss the feature around $3160 \pm 15 \text{ cm}^{-1}$. In the case of [C₂mim][NTf₂] and [C₈mim][NTf₂] the Raman and CARS spectra clearly indicate that it consists of two bands. In the corresponding IR spectra the band at $3160 \,\mathrm{cm}^{-1}$ exhibits a shoulder at its blue wing pointing also to two contributions but with an inversed intensity ratio compared to the CARS spectra, i.e. the band at longer wavelengths is now dominating. In the case of $[C_1 mim][NTf_2]$ all spectra reveal around $3180 \pm 15 \text{ cm}^{-1}$ only one band that is particularly clearly seen in the CARS spectrum (figure 5(c)). However, the band in the IR spectrum is red-shifted by about $10-20 \text{ cm}^{-1}$ with respect to the corresponding Raman and CARS bands. The cation of $[C_1 mim][NTf_2]$ has two methyl groups at the imidazolium ring and exhibits a mirror symmetry, whereas the two alkyl groups of the $[C_2 mim]$ and $[C_8 mim]$ cations are different from each other and the symmetry of the imidazolium ring is slightly broken (cf scheme 1). Therefore, it is likely that the differences between [C_1 mim] and the other two cations in the spectral region around 3160 cm⁻¹ are linked to the symmetry properties of the molecules and the different selection rules of the IR and Raman transitions. In the case of $[C_1 mim][NTf_2]$ the C(4)-H and C(5)-H stretching modes are completely equivalent as long as the environment does not break the symmetry. The corresponding normal modes should therefore be symmetric and anti-symmetric combinations of the C(4)–H and C(5)–H stretching vibrations. In principle, both modes can be Raman as well as IR active. However, from the calculations we know that the symmetric stretch is better seen in Raman, whereas the asymmetric stretch gives higher intensities in IR. Therefore, we identify the mode responsible for the Raman band at 3180 ± 15 cm⁻¹ with the symmetric and the mode causing the IR band at 3160 ± 15 cm⁻¹ with the anti-symmetric stretching vibration. In the case of $[C_2 mim][NTf_2]$ and $[C_8 mim][NTf_2]$ the symmetry is broken and both modes should carry Raman as well as IR intensity (cf figure 2). However, the disturbance of the symmetry is not very strong and the intensity distribution should still reflect the original symmetry (cf table 1). This is in accord with the observation that the Raman and CARS spectra of $[C_2mim][NTf_2]$ and [C₈mim][NTf₂] exhibit a weak Raman band slightly red-shifted with respect to the strong band



Figure 6. One-dimensional potentials (dashed) and probability densities for the lowest eigenstates (solid, equation (4)) of modes Q_2 and Q_3 (dimensionless coordinates, grid boundaries for other modes are chosen accordingly).

at $3180 \pm 15 \text{ cm}^{-1}$ which is missing in the [C₁mim][NTf₂] spectra, while the corresponding IR spectra show a shoulder in the blue wing of the band at $3160 \pm 15 \text{ cm}^{-1}$ which is absent in the case of [C₁mim][NTf₂]. Both bands are red-shifted with respect to the frequency of a free C(4/5)–H stretching mode of the imidazolium ring [27]. This indicates that both C–H groups are involved in weak HBs as indicated in figure 1.

The situation is different for the feature around $3120 \pm 15 \text{ cm}^{-1}$, which consists of two contributions in the case of all the investigated ILs and independent of the applied spectroscopic method. So it cannot simply be assigned to the C(2)–H stretching mode. The IR and Raman spectra reveal strong features around $1575 \pm 15 \text{ cm}^{-1}$ due to in-plane ring modes, indicating that nearby 3120 cm^{-1} overtones of these modes are expected. However, they should carry only low intensity and it would be surprising if the corresponding bands are of comparable strength to the fundamentals of the C–H stretching vibrations. But the overtones can mix with the C–H stretching modes and form Fermi resonances if the difference in frequency is small and the corresponding PES anharmonic (see below). Therefore, we conclude that the double structure results from the C(2)–H stretching vibration and possible Fermi resonances of C–H modes with overtones of the in-plane ring modes. Accordingly, the C(2)–H stretching mode is more red-shifted than the C(4)–H and C(5)–H stretching vibrations. This provides strong evidence that the C(2)–H group is involved in a stronger but still moderate HB.

5.2. Comparison with simulated spectra

In the following, we show that the assignment given above is also strongly supported by simulations of the spectra, which take anharmonicities into account. There are two effects shaping the IR spectrum in the CH-stretching range: firstly, the diagonal anharmonicity, which is partly due to H-bonding; and secondly, the Fermi resonance interaction of the CH-stretching fundamental and ring deformation overtone transitions. In figure 6 we show the anharmonic one-mode potentials for two representative modes together with the probability densities of the zero-order eigenstates. For the ring deformation mode Q_2 we notice a pronounced harmonic character (the same holds for Q_1 , not shown). The fundamental transition is calculated at 1621 cm^{-1} , which almost agrees with the harmonic value of 1616 cm^{-1} . For Q_1 we have 1611 cm^{-1} versus the harmonic value of 1606 cm^{-1} . Comparing these two values with the experimental spectrum, we observe a blue-shift. Since the experimental assignment is considered to be certain

(cf figure 3), we have scaled the two normal mode coordinates so as to obtain agreement with respect to the fundamental ring deformation transitions. Since Q_1 and Q_2 have an anharmonic IR intensity ratio of 0.75, a scaling of Q_2 to the lower frequency peak at 1569 cm⁻¹ and of Q_1 to the higher frequency peak at 1574 cm⁻¹ has been performed. In passing, we note that this scaling is in the range of what is usally applied when using DFT-based harmonic frequencies.

For the C(2)–H-stretching mode, Q_3 , a pronounced anharmonicity is observed in figure 6 causing a red-shift from the harmonic transition frequency of 3216 cm^{-1} down to 3093 cm^{-1} . Similar albeit smaller red-shifts are found for the other C–H stretching fundamental transitions.

The results of the anharmonic calculations are compiled in table 1. As far as the overtone transitions of the ring deformation modes at 3150 and 3140 cm^{-1} for Q_1 and Q_2 , respectively, are concerned we note that the effect of diagonal anharmonicity (mechanical and electronic) is essentially negligible, i.e. the overtone transitions have no noticeable intensity.

Next, we discuss the effect of a Fermi resonance interaction based on selected PES and DMS cuts. Here we focus on those mode combinations that give rise to some intensity in the ring deformation overtone transitions, see table 1. This includes the interactions between the pairs $(Q_1, Q_3), (Q_1, Q_4), (Q_2, Q_3)$, which can be rationalized by looking at the atomic displacements in figure 2. The main conclusion to be drawn from table 1 is that Fermi resonance interaction between *both* the C(2)–H and the C(5)–H stretching fundamental and the overtone transitions of the two ring deformation modes influences the absorption spectrum in the considered range.

The present theoretical results combine previous assessments of this spectral range which had a focus either on H-bonding in a cluster model [33] or on Fermi-resonance interaction in isolated imidazolium [27]. The effect of both, H-bonding and condensed phase 'packing', can be estimated by comparing with the gas phase imidazolium cation studied in [27]. These authors report anharmonic frequencies of 3181 cm^{-1} for the C(2)–H fundamental and 3196 and 3176 cm^{-1} for the in-phase and out-of-phase C(4,5)–H vibrations, respectively. Compared to the results given in table 1, we note that the situation is not clear-cut for the C(4,5)-H vibrations, but for the C(2)–H case a clear difference is observed and the red-shift of about 90 cm⁻¹ can be predominantly assigned to an effect of H-bonding on the O atom of the nearest NTf_2 anion. In passing, we note that this is in accord with the stronger acidicity of the C(2)-H site as compared with C(4/5)-H. Hence, the present calculations of anharmonic vibrational spectra performed for a $[C_2mim][NTf_2]$ cluster provide evidence for the combined effect of H-bonding and Fermi-resonance interactions. Only after inclusion of the diagonal anharmonicity are the CH-stretching fundamentals found in the range observed in the experiment. Further, accounting for the Fermi resonance coupling gives rise to a peak in the gap between the C(2)-H and the C(4/5)-H stretching fundamental transitions. Although the results are in semi-quantitative agreement with experiment, the present simple model does not provide the correct intensities. Inspecting the results obtained after inclusion of the diagonal anharmonicity in table 1, we note that the overtone transitions of the ring deformation modes are essentially in the middle of the gap formed by the C(2)–H and C(5)–H fundamentals. Having a gap of about 40–50 cm⁻¹, the conditions for Fermi resonance are rather unfavorable. Here slight changes might have a substantial effect on the oscillator strength. In principle, one could attempt to scale the CHstretching fundamentals with the goal of reproducing the spectra. While this procedure is applicable to the well assignable ring deformation fundamental transitions, it would render the model to become empirical in the CH-stretching region.

6. Summary and conclusions

The three different imidazolium-based ILs $[C_n mim][NTf_2]$ with n = 1, 2 and 8 have been studied applying IR, linear Raman and multiplex CARS spectroscopy and the results are compared with simulated anharmonic vibrational spectra based on five modes of a cluster consisting of four $[C_2 mim][NTf_2]$ ion pairs. The Raman band at $3180 \pm 15 \text{ cm}^{-1}$ and the IR band at $3160 \pm 15 \text{ cm}^{-1}$ are assigned to the more or less symmetric and anti-symmetric combinations of the C(4)–H and C(5)–H stretching vibration of the imidazolium ring. The feature around $3120 \pm 15 \text{ cm}^{-1}$ consists of two bands and results from the C(2)–H stretching mode and Fermi resonances of the C–H stretching vibrations with overtones of in-plane ring deformations. The calculations indicate that this feature cannot stem from pure overtones, since the PESs of the ring deformation modes are both nearly harmonic and their overtones should not have any intensity by themselves. In addition, the Fermi resonances are mainly due to coupling with the C(2)–H stretching mode. Our results strongly support the important role played by hydrogen bonding in ILs. In particular, it was found that the C(4)–H and C(5)–H groups are involved in weak HBs, while the HB of the C(2)–H group is somewhat stronger.

In conclusion, it was demonstrated that the combination of various vibrational spectroscopic techniques and anharmonic frequency calculations allows us to disentangle congested vibrational signatures.

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