

# Ultrafast structure and dynamics in ionic liquids: 2D-IR spectroscopy probes the molecular origin of viscosity

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# Water content

The water content in all samples was similarly low for all 2D-IR and viscosity measurements. Water content was measured before and after the laser experiments by FTIR spectroscopy. The peak absorbance of the H<sub>2</sub>O OH stretching-band was used as a vibrational marker of water contamination. In all experiments for all samples the water concentration was determined to be no greater than 150 ppm.

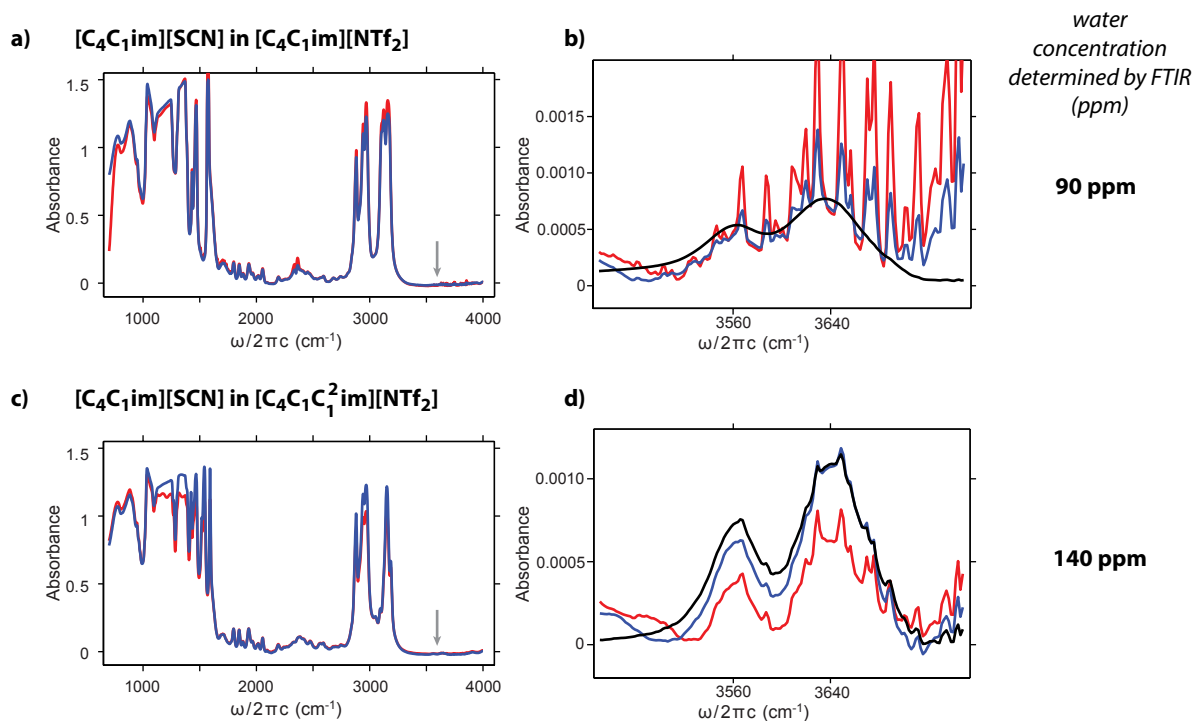


Figure 1: **Determination of water content in the 2D-IR experiments by FTIR spectroscopy.** **a)** FTIR of [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] shows a nearly flat region in the range of the OH stretch (arrow). **b)** The OH stretch intensity [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] before (red) and after (blue) the 2D-IR experiments was fit by nonlinear least squares to determine the maximum absorbance consistent with H<sub>2</sub>O. The 7 mOD absorption corresponds to 90 ppm H<sub>2</sub>O. **c)** FTIR of [C<sub>4</sub>C<sub>1</sub>C<sub>1</sub><sup>2</sup>im][NTf<sub>2</sub>] also shows a nearly flat region in the range of the OH stretch (arrow). **d)** The OH stretch intensity [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] before (red) and after (blue) the 2D-IR experiments was used to determine the maximum absorbance consistent with the presence of H<sub>2</sub>O. The 12 mOD absorption corresponds to 140 ppm H<sub>2</sub>O.

The OH-stretching band was fit by nonlinear least squares to OH-stretch of a ~1 wt % water loaded sample to determine the peak absorption consistent with the presence of

water. The peak OD was converted to concentration using the molar extinction of water  $100 \text{ M}^{-1}\text{cm}^{-1}$  (Venyaninov and Prendergast *Analytical Biochemistry* **248**, 234 (1997)). For the  $[\text{C}_4\text{C}_1\text{C}_1^2\text{im}][\text{NTf}_2]$ , the peak absorption was 12 mOD, and that gives a total weight of water per liter = 0.20 g/L. This number is then divided by the density of the IL, which is 1.44 kg/L (assuming it to be the same density as  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  as no literature value was found), and gives a weight fraction of  $1.4 \times 10^{-4} = 140 \text{ ppm}$ .

For the  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ , the peak absorption was 7 mOD, and that gives a total weight of water per liter of 0.13 g/L. This number is then divided by the density of the IL, which is 1.44 kg/L, which and gives weight fraction of  $9 \times 10^{-5} = 90 \text{ ppm}$ .

Water content was also determined by Karl Fischer titration before the viscosity measurements. We determined the water content to be in the range of 140 to 230 ppm for the  $[\text{C}_4\text{C}_1\text{C}_1^2\text{im}][\text{NTf}_2]$  samples and in the range of 160 to 280 ppm for  $[\text{C}_4\text{C}_1\text{C}_1^2\text{im}][\text{NTf}_2]$ . On the available instrument, replicate measurements give variation in water content as large as 50 ppm. Even with the error bar associated with the measurement, this determination agrees with the FTIR spectroscopy in magnitude and the trend (slightly higher water in the  $[\text{C}_4\text{C}_1\text{C}_1^2\text{im}][\text{NTf}_2]$ ).

**Table 1: Water content in samples as determined by Karl Fischer titration. Multiple runs of the same sample on the same instrument show variation on the 50 ppm level. Nevertheless all measurements were in the range of 100 – 300 ppm.**

Sample	Run	Water (ppm)
$[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$	1	207
	2	157
+ 30 mM SCN	1	287
	2	256
$[\text{C}_4\text{C}_1\text{C}_1^2\text{im}][\text{NTf}_2]$	1	143
	2	173
+ 30 mM $[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$	1	227
	2	181

Water content in the few hundred ppm range is reasonable for our determination of viscosity and dynamics. First, the viscosities that we measure compare very well with literature

values (considering the spread in the literature). Second, the viscosity of  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  changes slowly with water content (considering the trace amounts we are discussing). For example, one can estimate that the viscosity should change by only 0.5% at 200 ppm water content ( $x_{\text{H}_2\text{O}} = 0.0045$ ) by linear interpolation within the data of Canongia Lopes et al *J Phys Chem B*, **115**, 6088 (2011).

## Viscosity

The viscosities of the ILs are unaffected by the 30 mM concentration of the thiocyanate. The viscosity of neat  $[\text{C}_4\text{C}_1\text{C}_1^2\text{im}][\text{NTf}_2]$  is  $99.7 \pm 0.1$  cP and the mixture is  $99.3 \pm 0.1$  cP; similarly the viscosity of  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  is  $50.1 \pm 0.1$  cP and the mixture is  $50.2 \pm 0.1$  cP. These viscosity measurements are within the range of viscosities reported in the literature (see Hunt JPCB 2007 for a summary); our measurement for  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  agree exactly with the report from Canongia Lopes et al *J Phys Chem B*, **115**, 6088 (2011).

## Long time spectra

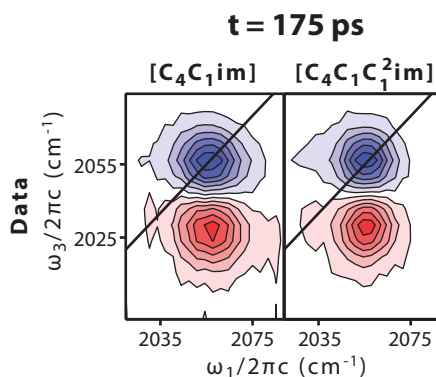


Figure 2: **Decay of correlation** Spectra at 175 ps show the decay of frequency correlation to 0 within error for both ionic liquids.