

Supporting Information

Interaction of Levitated Ionic Liquid Droplets with Water

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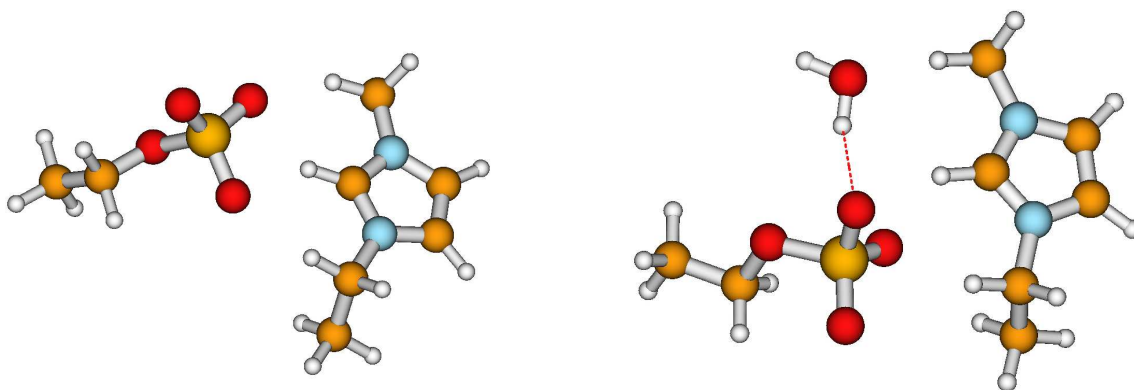


Figure S1: Calculated structures (B3LYP/6-31+G*) of [EMIM][EtSO₄] and [EMIM][EtSO₄] with one water molecule optimized¹ from starting structures according to Dhumal et. al.² for [EMIM][EtSO₄] and to Zhang et al.³ and Köddermann et al.⁴ for [EMIM][EtSO₄] with one water molecule.

Table S1: Selected calculated harmonic wavenumbers, IR band strength and Raman scattering cross sections (B3LYP/6-31+G*) for the structures shown in Figure S1.

vibration	[EMIM][EtSO ₄]			[EMIM][EtSO ₄]+H ₂ O		
	ω/cm^{-1}	$I_{\text{IR}}/\text{km mol}^{-1}$	$\sigma_{\text{Raman}}/10^{-36} \text{ m}^2 \text{ sr}^{-1}$	ω/cm^{-1}	$I_{\text{IR}}/\text{km mol}^{-1}$	$\sigma_{\text{Raman}}/10^{-36} \text{ m}^2 \text{ sr}^{-1}$
O-S-O bend.	525	15	24	527	35	22
O-S-O wag.	540	44	14	541	44	10
S-O-C ₂ H ₅ stretch	732	258	73	745	230	59
sym. O=S=O stretch	983	284	102	984	340	85
O=S=O stretch	1235	441	15	1217	351	9

asym. (O)-CH ₂ -CH ₃ stretch	3044	25	9	3054	29	47
(N)-CH ₃ stretch	3075	41	97	3060	56	101
C2-H stretch	3216	658	79	3162	276	22
				3166	198	66
sym. C4,5-H stretch	3315	1	53	3317	1	49

Table S2: Comparison of the experimentally observed wavenumbers for [EMIM][EtSO₄] under dry atmosphere conditions and differences between the spectra recorded under humid and dry conditions (Raman and IR spectra) in comparison to the differences between the calculated wavenumbers for [EMIM][EtSO₄] and [EMIM][EtSO₄]+H₂O ($\Delta\omega$).

Raman shift (dry)/ cm ⁻¹	Δ Raman shift (humid-dry)/ cm ⁻¹	$\tilde{\nu}$ (IR, dry)/ cm ⁻¹	$\Delta\tilde{\nu}$ (IR, humid-dry)/ cm ⁻¹	$\Delta\omega$ / cm ⁻¹
565	3	567		2
578	4	578	0	1
765	15	768	7	13
1022	0	1020	-4	1
1225	-6	1227	-8	-18
2905	2	2901	5	10
2968	0	2982	5	-15 ^a
3106	8	3105	6	^a
3158	8	3151	2	2

^a The pronounced wavenumber differences between the C-H stretching vibrations of [EMIM][EtSO₄] and [EMIM][EtSO₄]+H₂O can be explained with the structural difference especially in the region of the (N)-CH₃ group (see Figure S1). Furthermore, the calculations reflect only gas phase structures without additional intermolecular interactions which occur in the bulk liquid and harmonic frequency calculations without anharmonic contributions such as Fermi resonances.⁵

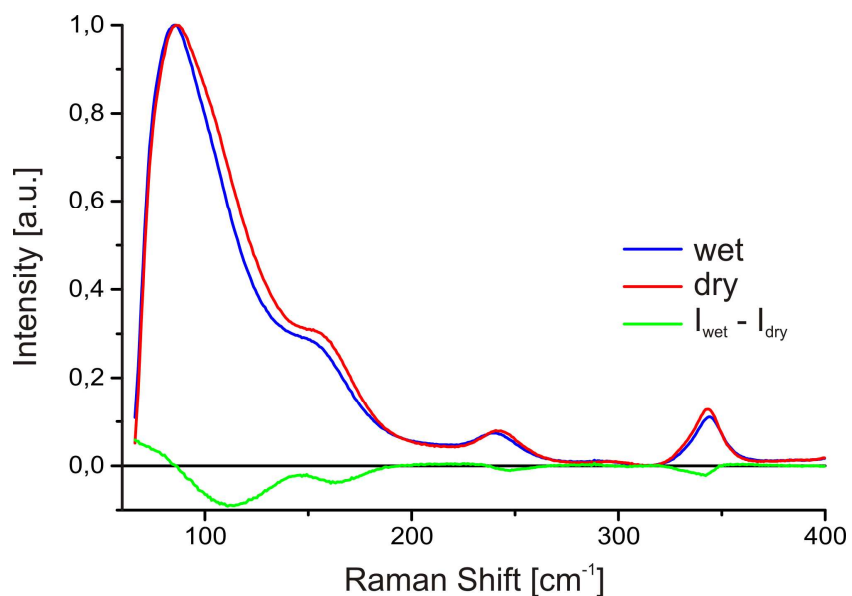


Figure S2: Raman spectra of [EMIM][EtSO₄] (normalized intensity) in the region of 50–400 cm⁻¹ under humid and dry conditions and the difference spectrum between both spectra.

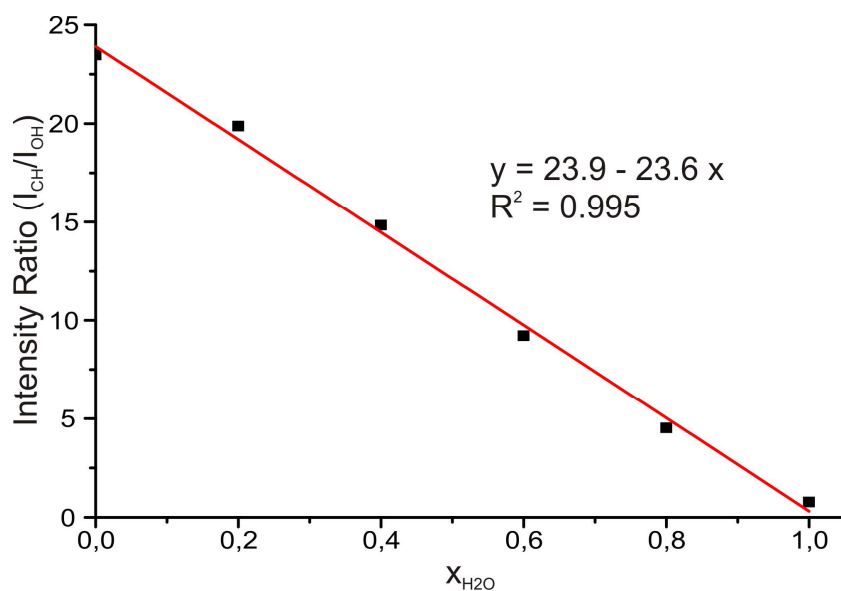


Figure S3: Ratio of the integral over the CH bands of [EMIM][EtSO₄] (2783–3193 cm⁻¹) to the integral over the H₂O band (3257–3771 cm⁻¹) for mixtures of [EMIM][EtSO₄] with H₂O in different mole fractions. The calibration curve can be used to calculate the mole fraction of water in the ionic liquid ($x=x_{H_2O}$) by the ratio of the integrals of the areas of the bands of the CH stretching vibrations of the ionic liquid and the OH stretching vibration of the water.

References:

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