Supplementary Information (SI) for Physical Chemistry Chemical Physics.

H-bonding Structures of 1-Ethyl-3-methylimidazolium Trifluoroacetate: A Vibrational Spectroscopic Study

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A. Trace water present in the ionic liquid: We have exploited the OH stretching regime of water (3200 to 3800 cm^{-1}) to estimate the water content of the ionic liquid, which was found to be around 0.2 MF. A recent study[1] on solitary water in a number of Emim cation based ionic liquids and dipolar solvents has shown that around this level (or below) of dilution the water molecules remain mostly in the monomeric form and retain a structure like anion…H-O-H….anion, although the singly anion bound water (anion…H-O-H type) also exists but comparatively lesser in proportion.[1,2] Moreover, linear correlations among the OH stretching modes of doubly bound (ν_1, ν_2, ν_3, and ν_4) and singly bound (ν_4 and ν_5) water molecules in this type of trace water containing ionic and dipolar solvent medium have been observed. Figure S2 displays the spectral decomposition of the OH stretching regime for undoped [Emim:TFA]. Interestingly all five modes, ν_1, ν_2, ν_3, ν_4 and ν_5, can be found here also; similar to what was previously reported for 1-hexyl-3-methylimidazolium chloride/iodide.[1] Next, we verified whether the estimated frequency values obey the proposed empirical relation in that same work. Table S3 presents a comparison between the peak frequencies obtained from fits and the peak frequencies calculated employing the empirical relations noted above. Note that to calculate the peak frequencies using those correlations we have used the ν_3 (3502 cm^{-1}) value from our fit and estimated the other frequencies. This comparison shows good agreement and suggests that most of the water molecules in this ionic liquid are in monomeric form.

Moreover, NMR data for Emim:TFA indicates an even lower content (< 0.1 mole fraction) of trace water in the neat ionic liquid than what we estimate using linear spectroscopy. The NMR measurements were carried out in a 400 MHz NMR spectrometer (Advance NEO, Bruker). The observed higher tracer water content in the linear IR measurements than the actual water content of the sample, as measured by NMR spectroscopy, is probably due to the accumulation of excess atmospheric water by the ionic liquid during the sample transfer to the linear IR cell in the laboratory environment. Dealing with a tiny volume of sample and following the drop-casting technique makes the solvent transfer in the linear IR method more vulnerable towards atmospheric water than NMR. The chemical shift value for the water molecules has been found to be ~ 3 ppm and it agrees well with the recently reported[3] correlation between the chemical shift value and OH stretching frequency of solitary water in ionic and dipolar solvent. Thus, application of both linear IR and NMR techniques suggests that water molecules in Emim:TFA are mostly monomeric in nature.

B. Analysis of the pump slices and estimated anharmonicity values: In order to determine the diagonal peak pairs, we have considered that the most intense positive and negative peaks, along the pump axes, of time-zero co-polarized 2DIR spectra are the diagonal pairs. Representative pump slices are presented in figure 3 and S5. The pump slices were fit using multi-Gaussian model and the extracted peak frequencies were utilized to estimate the diagonal anharmonicity values for each diagonal feature. The estimated anharmonicity values of the three diagonal peaks range from ~ 18 cm^{-1} (for the peak centered at ω_1=1679cm^{-1} and the peak centered at ω_1=1687 cm^{-1}) to ~ 24 cm^{-1} (for the peak centered at ω_1=1698 cm^{-1}). The previously reported anharmonicity value for this vibrational mode of TFA anion in the NaTFA and water mixture is ~ 16 cm^{-1}, [4] while for TFA-methylguanidinium salt bridge in dimethyl sulfoxide solvent the value is ~ 18 cm^{-1}.[5] Furthermore, for acetic acid in carbon tetrachloride and sodium acetate in D_2O, the anharmonicity ranges from ~ 20 cm^{-1} to 27 cm^{-1};[6,7] therefore, our observed anharmonicity values agree with previous measurements.

Now to talk about the other features on the 2DIR spectra we assign them as (ω_1, ω_3), (where ω_1 and ω_3 are their approximate pump and probe frequencies, respectively), based on their location on the spectra. Due to their complex shapes and significant overlapping with other peaks, the off-diagonal features are relatively harder to dissect than the diagonal features. According to our initial analysis of the Tw-dependent data the 1687 and 1698 cm^{-1} peaks result (1690, 1675), (1690, 1700), and (1700, 1665), (1700, 1690) cross peak pairs. Close similarity between the diagonal and off diagonal anharmonicities (~ 20 cm^{-1}) indicates a strong coupling between these two modes. Please note that we refrain from making any comments on the off-diagonal peak features that are below ω_1=1685 cm^{-1} as we need further experimental and theoretical studies, which are still underway, to assign their correct origin and nature.

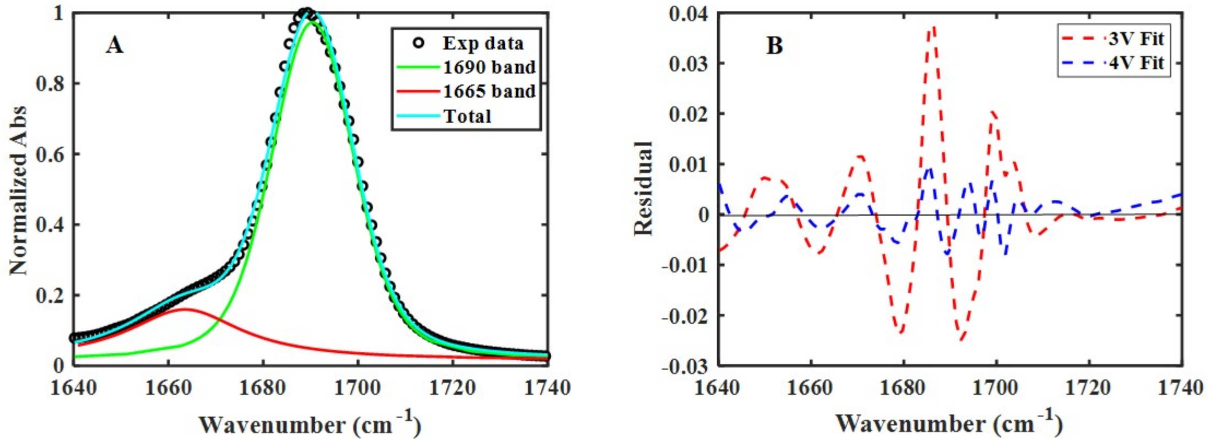


Figure S1. A) Fit of Asymmetric carbonyl stretching band using 2-Voigt fit model are shown in solid lines. B) Comparison between the residuals of 2-Voigt and 3-Voigt fits. Plots are color coded.

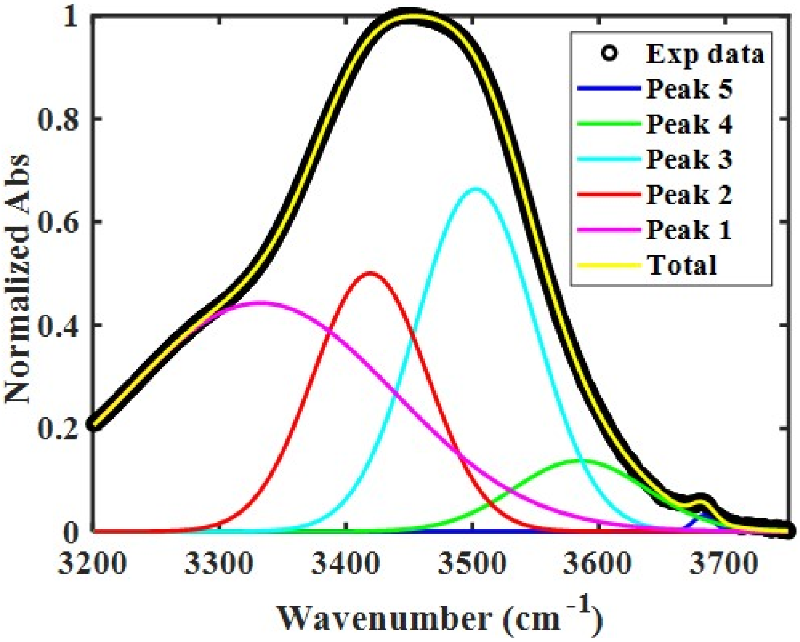


Figure S2. Spectral decomposition of the OH stretching regime for undoped Emim:TFA (black open circles) and corresponding multi-Voigt fit is shown in solid lines. The fit is color coded.

Table S3. The peak frequencies values (2nd row) obtained from our fit (figure S2) and the peak frequencies (1st row) obtained by employing the v3 value (3502 cm^{-1}) in the correlations reported in the figure 8 of reference 1. The frequency values presented in the table all are in cm^{-1} unit.

Data	**v1**	**v2**	**v3**	**v4**	**v5**
Lit	3359	3425		3582	3677
Our	3332	3419	3502	3585	3682

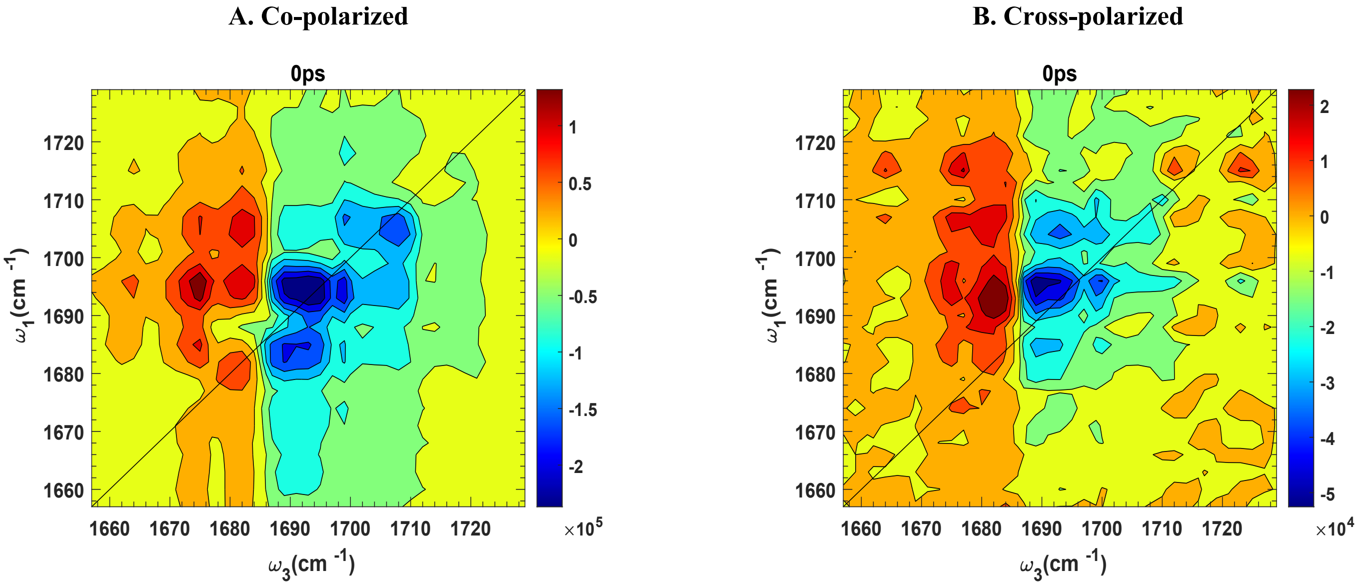


Figure S4. 2DIR spectra of asymmetric carbonyl stretching band in two different polarizations (A. Co-polarized and B. Cross-polarized) at zero-time delay between the pump and probe, i.e. $T_w = 0$. Black continuous line represents the actual diagonal line. ω_1 and ω_3 represents the pump and probe axes, respectively.

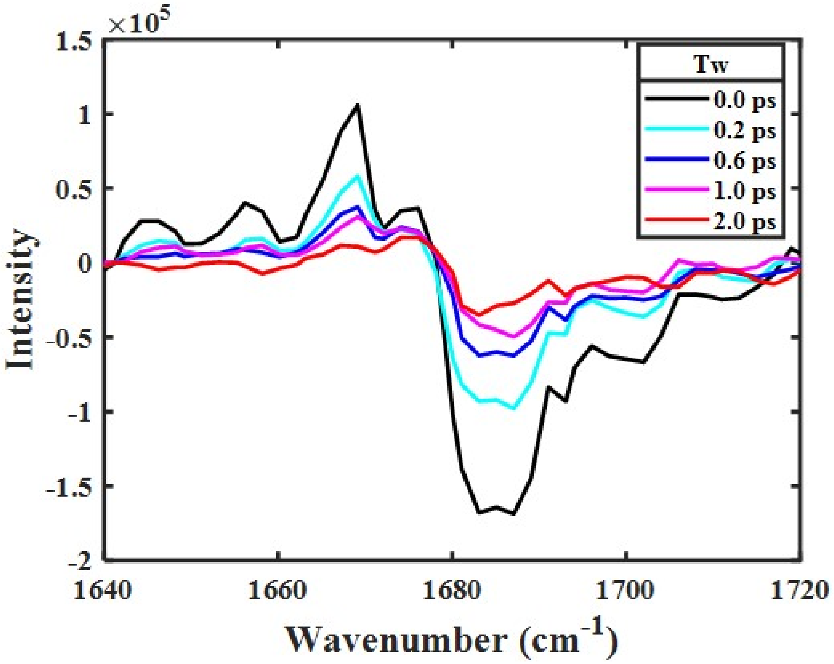


Figure S5. Pump slices along 1679 cm^{-1} for co-polarized 2DIR spectra of neat Emim:TFA at different Tw values. The plots are color-coded.

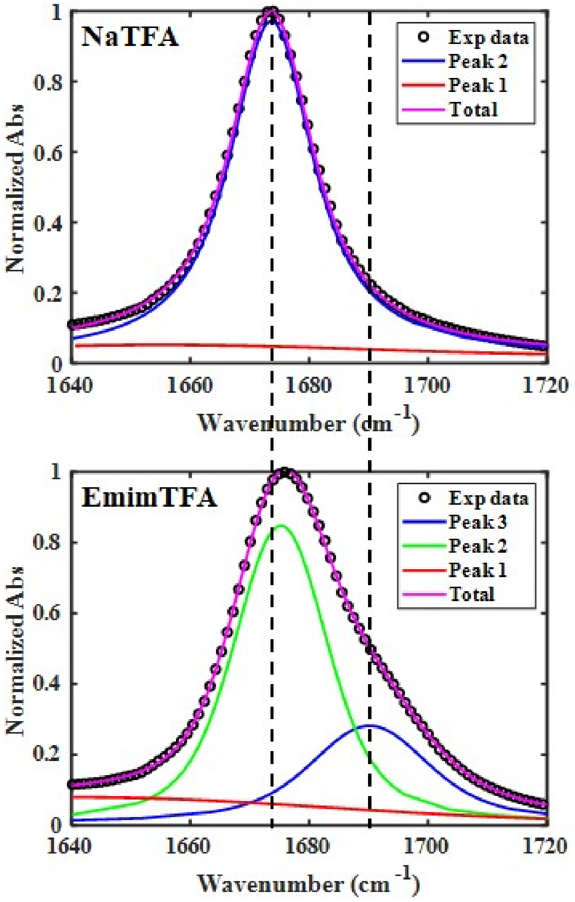


Figure S6. Comparison between the deconvoluted spectra of asymmetric carbonyl stretching band for NaTFA (upper panel) and Emim:TFA (bottom panel) in a representative protic solvent D_2O. Plots are color-coded.

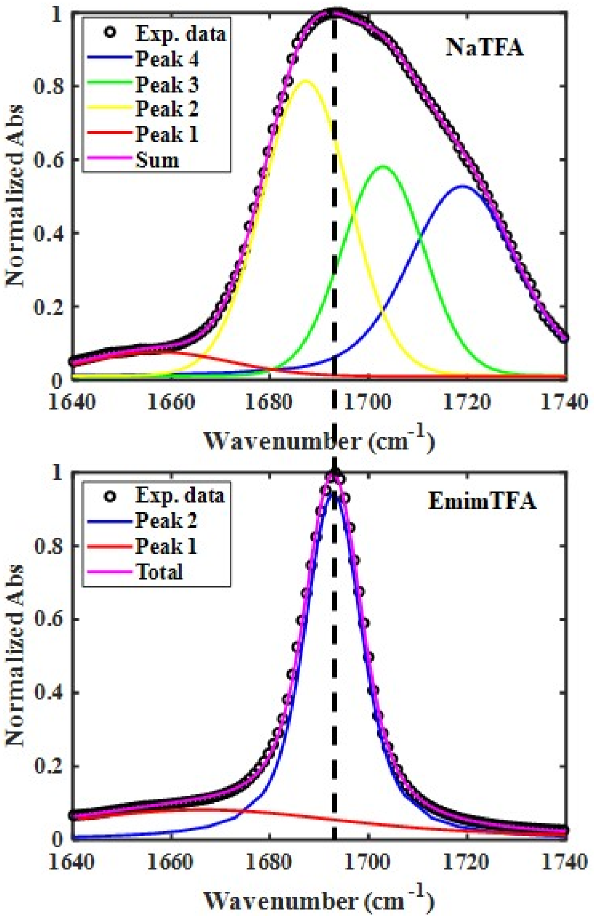


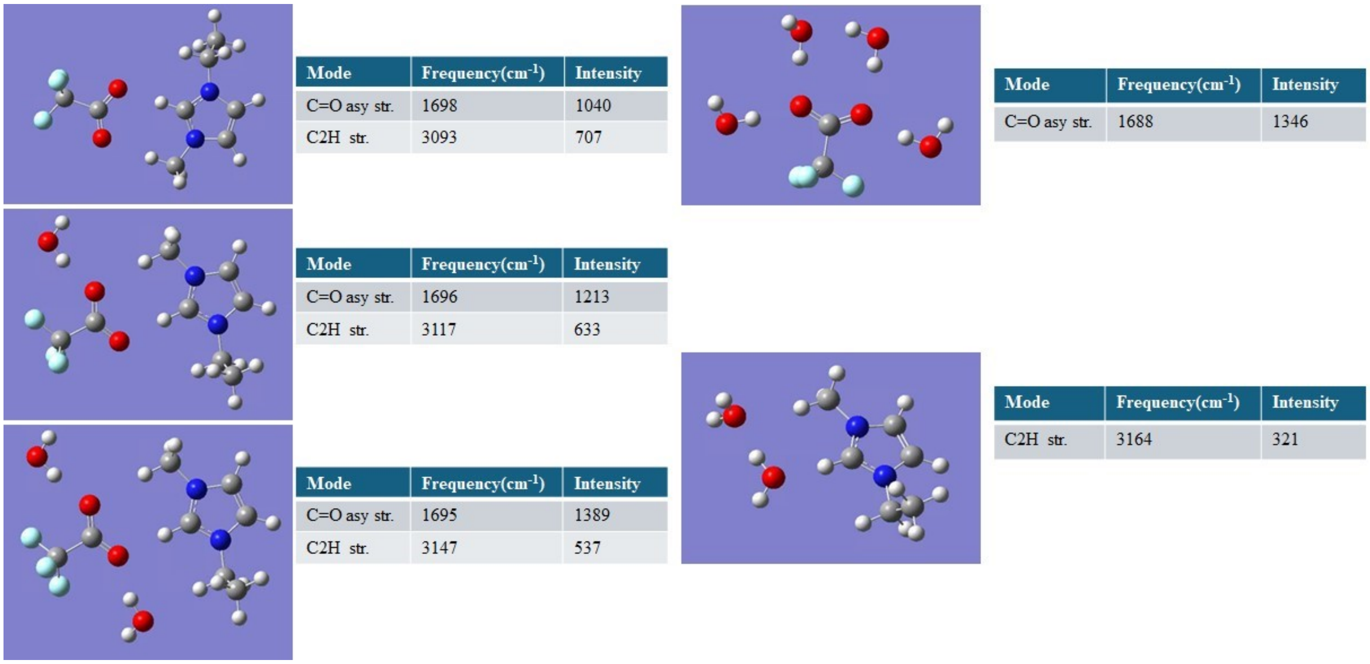
Figure S7. Comparison between the deconvoluted spectra of asymmetric carbonyl stretching band for NaTFA (upper panel) and Emim:TFA (bottom panel) in a representative aprotic solvent acetonitrile. Plots are color-coded.

Table S8. The frequency values and corresponding amplitudes obtained from the deconvolution of the asymmetric carbonyl stretching band in four different solvents for Emim:TFA and NaTFA. The same parameters for the undoped Emim:TFA is also tabulated here. Amplitude and frequency value of the corresponding peak is depicted in a(N) and f(N) columns, respectively, where N = 1 to 5.

Solvent	Salt	a1 (%)	f1	a2 (%)	f2	a3 (%)	f3	a4 (%)	f4	a5 (%)	f5
EmimTFA	EmimTFA	44	1672			28	1688	28	1697		
Acetonitrile	EmimTFA	16	1658			84	1693				
	NaTFA	5	1657			37	1687	25	1703	33	1719
DMSO-d6	EmimTFA	22	1646			78	1692				
	NaTFA	13	1667			79	1692	8	1701		
MeOH-d4	EmimTFA	8	1645	55	1676	37	1690				
	NaTFA	5	1646	63	1676	32	1690				
DOD	EmimTFA	21	1641	55	1675	24	1690				
	NaTFA	17	1655	83	1674						

Table S9. The frequency values obtained for asymmetric carbonyl stretching mode of TFA$^-$ and C2H stretching frequencies from DFT calculations of Emim:TFA and NaTFA, employing different calculation methods.

Ion/Ion Pairs	**Implicit Solvent**	**Explicit Solvent**	**Calculated Asymmetric Carbonyl Stretching Frequency (cm^{-1})**	**Calculated C2H Stretching Frequency (cm^{-1})**	**Corresponding Linear IR Asymmetric Carbonyl Stretching Frequency (cm^{-1})**
TFA$^-$ anion	None	None	1762		
Emim$^+$ cation	None	None		3297	
EmimTFA (C2H)	None	None	1717	2770	
EmimTFA (C2H)	DMSO	None	1699	3090	1692
EmimTFA (C2H)	Acetonitrile	None	1699	3088	1693
EmimTFA (C2H)	Acetonitrile	3 Acetonitrile Molecules	1698	3116	
NaTFA	None	None	1676		
NaTFA	DMSO	None	1684		1692
NaTFA	None	3 DMSO Molecules	1719		
NaTFA	DMSO	3 DMSO Molecules	1694		
NaTFA	Acetonitrile	None	1684		1687
NaTFA	Acetonitrile	3 Acetonitrile Molecules	1690		



Mode	Frequency(cm^{-1})	Intensity
C=O asy str.	1698	1040
C2H str.	3093	707

Mode	Frequency(cm^{-1})	Intensity
C=O asy str.	1696	1213
C2H str.	3117	633

Mode	Frequency(cm^{-1})	Intensity
C=O asy str.	1695	1389
C2H str.	3147	537

Mode	Frequency(cm^{-1})	Intensity
C=O asy str.	1688	1346

Mode	Frequency(cm^{-1})	Intensity
C2H str.	3164	321

Figure S10. Effect of water (D_2O) addition on a representative single ion pair (left panel) until hydrated individual ions (right panel). The table beside each figure depicts the calculated asymmetric carbonyl stretching and C2H stretching frequency values and corresponding intensities. Water was applied as dielectric continuum for these calculations. The number of water molecules around the cation and the anion incorporated in these hydrated ion calculations (right panel) were based on the earlier dielectric relaxation spectroscopic studies[8,9] of similar systems.

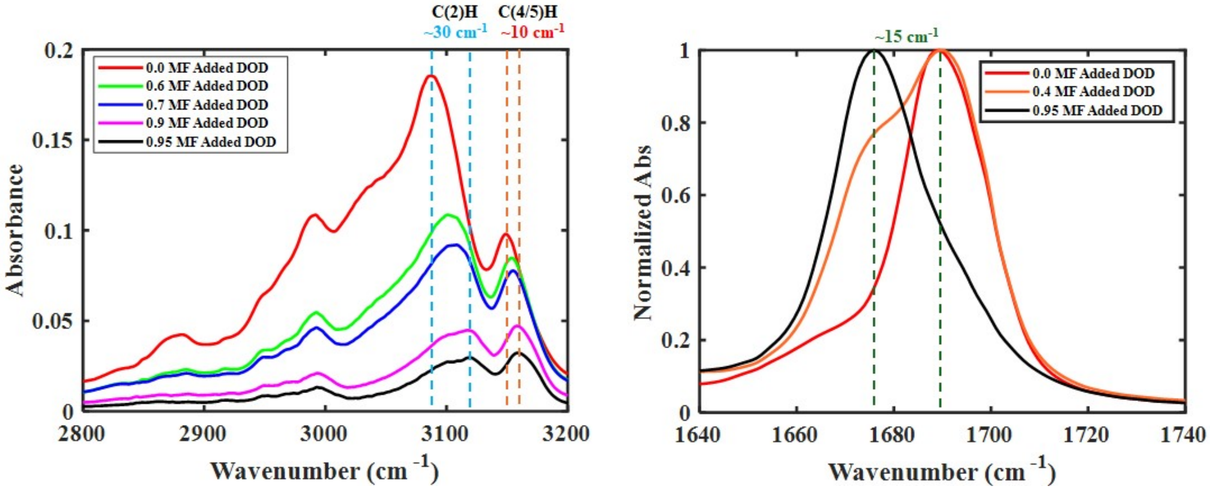
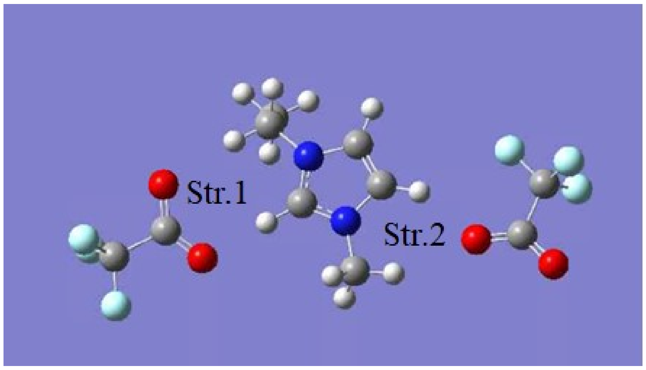
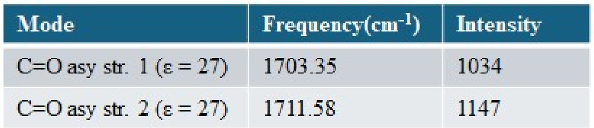


Figure S11. The C-H stretching regime and asymmetric carbonyl stretching regime of Emim:TFA/D_2O system with varying water concentration. The peak shifts of the C(2)-H and C(4/5)-H stretching modes are specified with the cyan and orange broken lines, respectively. The green broken lines in the right panel figure indicate the frequency shift of asymmetric carbonyl stretching band for three different water concentrations. Water concentrations are color coded.





Mode	Frequency(cm^{-1})	Intensity
C=O asy str. 1 (ε = 27)	1703.35	1034
C=O asy str. 2 (ε = 27)	1711.58	1147

Figure S12. Representative optimized configuration of triple ion structure. The table beside the figure depicts calculated frequency values and corresponding intensities of asymmetric carbonyl stretching modes.

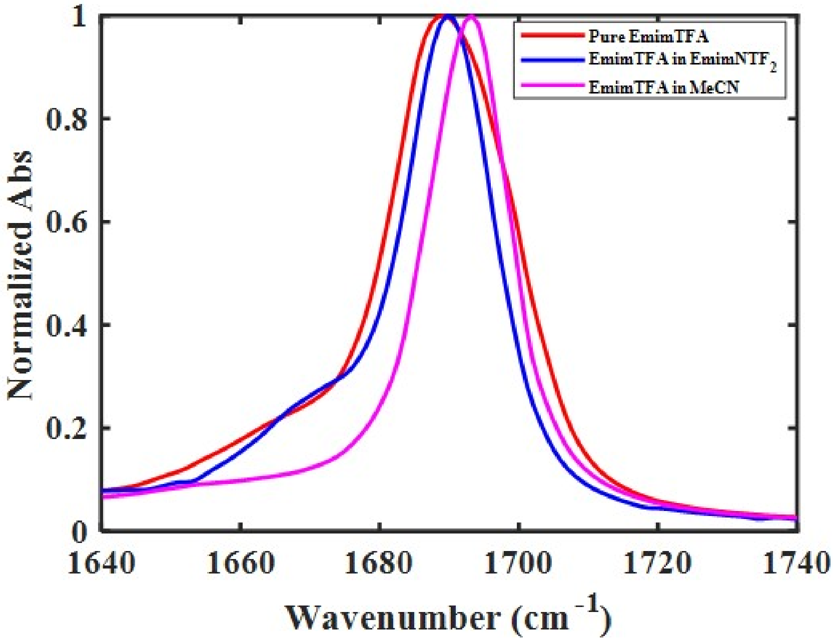


Figure S13. The asymmetric carbonyl stretching spectra of undoped Emim:TFA (Red) and Emim:TFA in two representative diluting solvent media, Emim bis(trifluoromethylsulfonyl)imide (Emim:NTF$_2$, Blue) and acetonitrile (Pink). The concentration of Emim:TFA was <0.1 MF in the diluted systems. Plots are color-coded.

References:

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