

C-D Vibration At C-2 Position Of Imidazolium Cation As A Probe Of The Ionic Liquid Microenvironment.

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S1. NMR of C-2D labeled imidazolium-based ionic liquids.

All synthesized products were dried for 24 h at 80 °C under high vacuum before spectroscopic measurements. NMR measurements were taken on a Bruker 300MHz high-resolution spectrometer

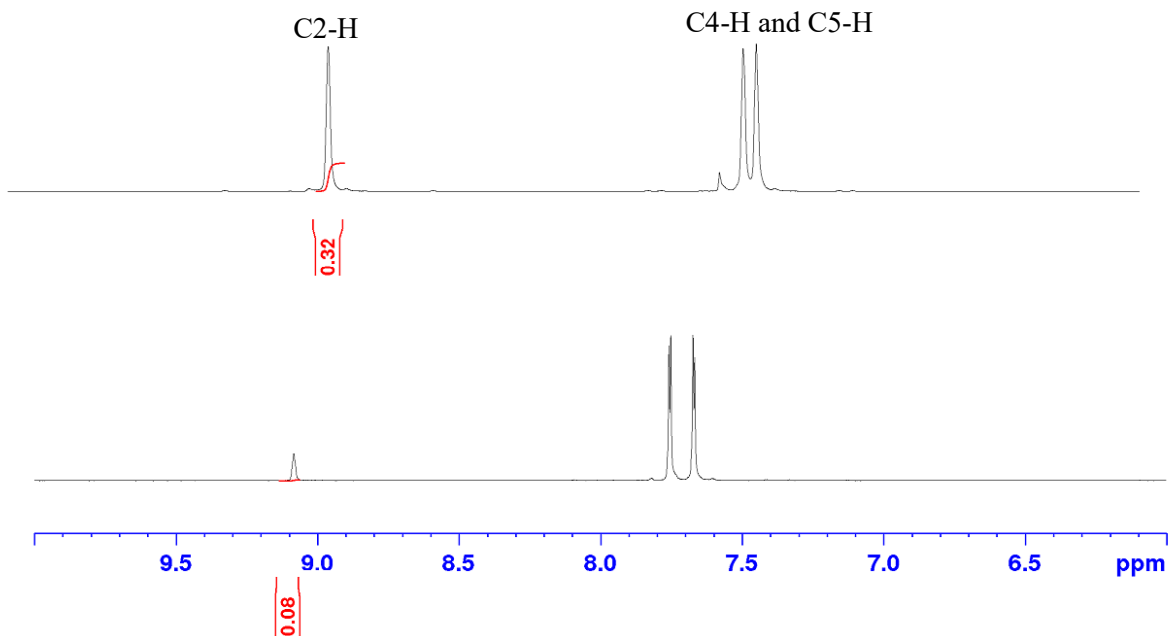


Figure S1: Typical changes in NMR spectrum before (top) and after conversion (bottom) to C2-D-labeled product. Notice that the integrated area (red) is significantly lower after conversion. The integrated area was compared to methyl protons at C-3 position of the imidazolium cation.

NMR Data:

1-Ethyl-3-methyl-[D1]imidazolium Tetrafluoroborate [EMIM][BF₄].

¹H-NMR (300 MHz, CDCl₃/ DMSO): δ = 8.92 (s, 0.10H), 7.45(s, 1H), 7.26(s, 1H), 4.27(q, 2H), 3.82(s, 3H), 1.59 (t, 3H)ppm.

1-Hexyl-3-methyl-[D1]imidazolium tetrafluoroborate [HMIM][BF₄].

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.52(s, 0.03H), 7.76(s, 1H), 7.69(s, 1H), 4.14(t, 2H), 3.84(s, 3H), 1.77(q, 2H), 1.22-1.30 (m, 6H), 0.86(s, 3H) ppm.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][Tf₂N].

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.08 (s, 0.24H), 7.76(s, 1H), 7.67(s, 1H), 4.19(q, 2H), 3.83(s, 3H), 1.40 (s, 3H) ppm.

1-Hexyl-3-methyl-[D1]imidazolium bis(trifluoromethylsulfonyl)imide [HMIM][Tf₂N].

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.05(s, 0.09H), 7.73(s, 1H), 7.69(s, 1H), 4.10(q, 2H), 3.82(s, 3H), 1.76(q, 2H), 1.25-1.30(m, 6H), 0.84 (s, 3H) ppm

1-Ethyl-3-methyl-[D1]imidazolium trifluoromethanesulfonate [EMIM][CF₃ SO₃].

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.08(s, 0.33H), 7.76(s, 1H), 7.68(s, 1H), 4.17(q, 2H), 3.84(s, 3H), 1.41(s, 3H) ppm

1-Hexyl-3-methyl-[D1]imidazolium trifluoromethanesulfonate [HMIM][CF₃SO₃].

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.09(s, 0.05H), 7.76(s, 1H), 7.69(s, 1H), 4.16(s, 1H), 3.85(s, 3H), 1.78(q, 2H), 1.27-1.33 (m, 6H), 0.87(s, 3H) ppm

1-Ethyl-3-methyl-[D1]imidazolium tris(pentafluoroethyl)trifluorophosphate [EMIM][FAP]

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.11(s, 0.01H), 7.76(s, 1H), 7.68(s, 1H), 4.19 (q, 2H), 3.83(s, 3H), 1.40 (t, 3H) ppm.

1-Hexyl-3-methyl-[D1]imidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM][FAP]

¹H-NMR (300 MHz, [D6]DMSO): δ = 9.09 (s, negligible H), 7.76 (s, 1H), 7.69(s, 1H), 4.15(t, 2H), 3.85(s, 3H), 1.78(m, 2H), 1.27(m, 6H), 0.87(t, 3H) ppm

1-Ethyl-3-methyl-[D1]-imidazolium ethylsulfate [EMIM][EtSO₄].

¹H-NMR (300 MHz, [D6]DMSO): δ = 8.69(s, 0.23H), 7.46(s, 1H), 7.40(s, 1H), 4.22(q, 2H), 4.10(q, 2H), 3.87(s, 3H), 1.48(t, 3H), 1.20 (t, 3H) ppm.

S2. Synthesis of C4-D and C5-D labeled [EMIM][BF₄].

The reactions were carried exactly in similar condition as described in the text of the manuscript except that the reaction was run for at least a week and sodium deuterioxide was added to the mixture in catalytic amount. Water (H₂O) was added to protonate the C2-position. Our results show that the NMR proton signal from the C4- and C5- position is significantly reduced after conversion. In the FTIR, we observe two peaks. We observed similar NMR and IR spectral features for other C4-D and C5-D labeled ionic liquids investigated in this work.

C4-D and C5-D labeled [EMIM][BF₄]

¹H-NMR (300 MHz, CDCl₃/ [D6] DMSO): δ = 8.92 (s, 0.95 H), 7.45(s, 0.22H), 7.26(s, 0.26H), 4.27(q, 2H), 3.82(s, 3H), 1.59 (t, 3H) ppm

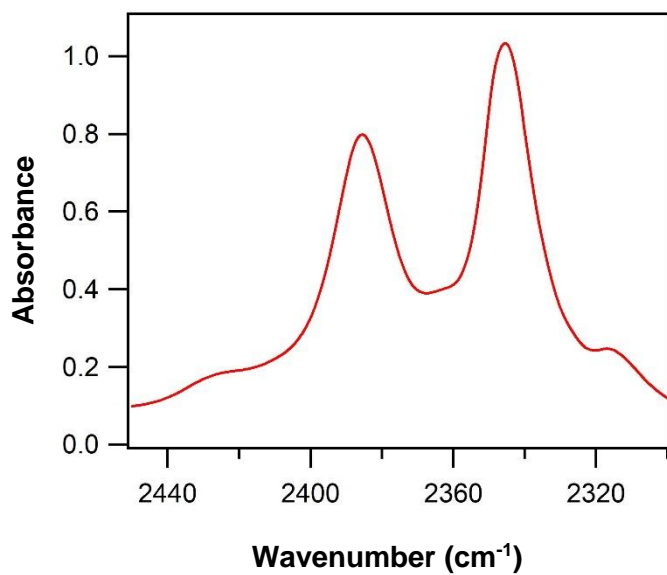


Figure S2. FTIR of C4- and C5-labeled [EMIM][BF₄] with split signature around 2300 cm⁻¹. The location of the peaks are similar across different ionic liquids.

S3. Representative FTIR of an ionic liquid and its analysis

The water content of the ionic liquids was determined through the “free water” bands at 3640 and 3560 cm^{-1} . The peak absorbance of this OH stretching region of water for every liquid was converted to concentration using molar extinction of water ($100 \text{ M}^{-1} \text{ cm}^{-1}$).¹ This number was divided by the density of the ionic liquid, as given in literature, to determine the water content in parts per million (ppm). Analysis of test samples used for linear and 2D-IR measurements show that the water concentration ranged approximately between 100 to 800 ppm in our tested samples. As an example, we show the spectrum of C-2D labeled [EMIM][BF₄] with the “free water” bands.

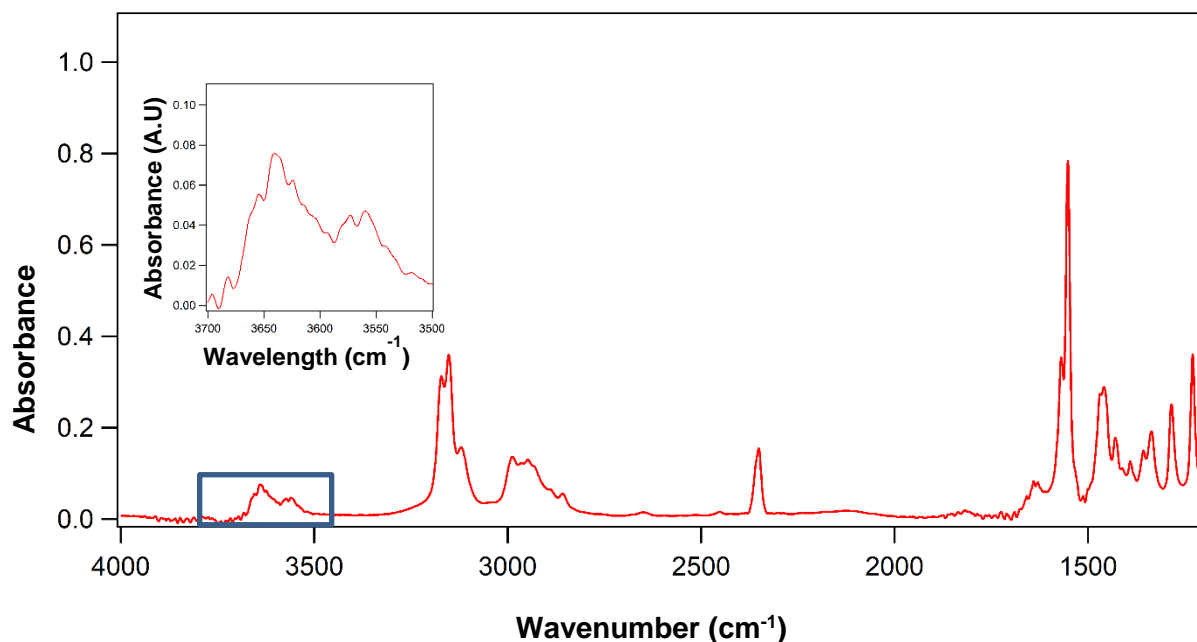


Figure S3. FTIR of C-2D [EMIM][BF₄] with a clear signature C-2D signature between 2500 cm^{-1} to 2500 cm^{-1} . The inset shows the OH region indicating the presence of “free water” in the liquid.

To calculate the extinction coefficient, we first calculated the molarity of the ionic liquid. In case of [EMIM][BF₄], the concentration of pure liquid is 7.13 M. However, our conversion of pure liquid to C2-D product was found to be ~90% by NMR. So, the effective concentration of the product was 6.42M. This solution was diluted with native [EMIM][BF₄] to a concentration of 0.5 M. Approximately, 10 μL of this liquid was placed between two CaF₂ windows separated by 25 μm spacer and sealed in a gastight dismountable liquid cell holder (Pike Technologies). Using Beer-Lambert law, we calculated the extinction coefficient to be $\sim 145 \text{ M}^{-1} \text{ cm}^{-1}$.

The extinction coefficient of the C2-D band was similar for all the ionic liquid investigated this work ($\sim 150 \text{ M}^{-1} \text{ cm}^{-1}$).

¹Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.*, **2001**, 3, 5192-5200.

S4. DFT calculations of the C-D spectrum of the investigated ionic liquids.

Calculation show that there is a relationship between hydrogen bond length, the angle, and the vibrational frequency of the C2-D mode. We see similar trend our experimental exploration indicating that hydrogen bonding has a role to play in the observe shifts.

Table S4. Calculated hydrogen bond lengths, angles, and vibrational frequencies from ω -B97XD/def2-TZVP harmonic analysis of EMIM-based ionic liquids

Anion	D...Y Å	C-D...Y degrees	$\nu(\text{calc})$ cm^{-1}
EtSO ₄	2.00	172.9	2355
CF ₃ SO ₃	2.07	178.2	2391
Tf ₂ N	2.19	175.5	2412
BF ₄	2.28	142.1	2453

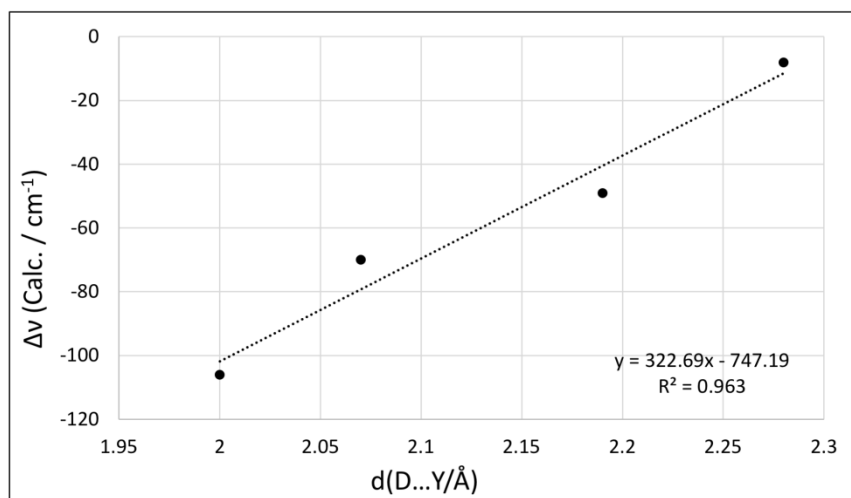


Figure S4(a). Correlation between calculated harmonic vibrational frequencies and hydrogen bond lengths involving C(2)-D...Y (Y=O,N,F) in complexes involving EMIM and EtSO₄ (far left), CF₃SO₃, Tf₂N, and BF₄ (far right). FAP fails to form a hydrogen bond with EMIM.

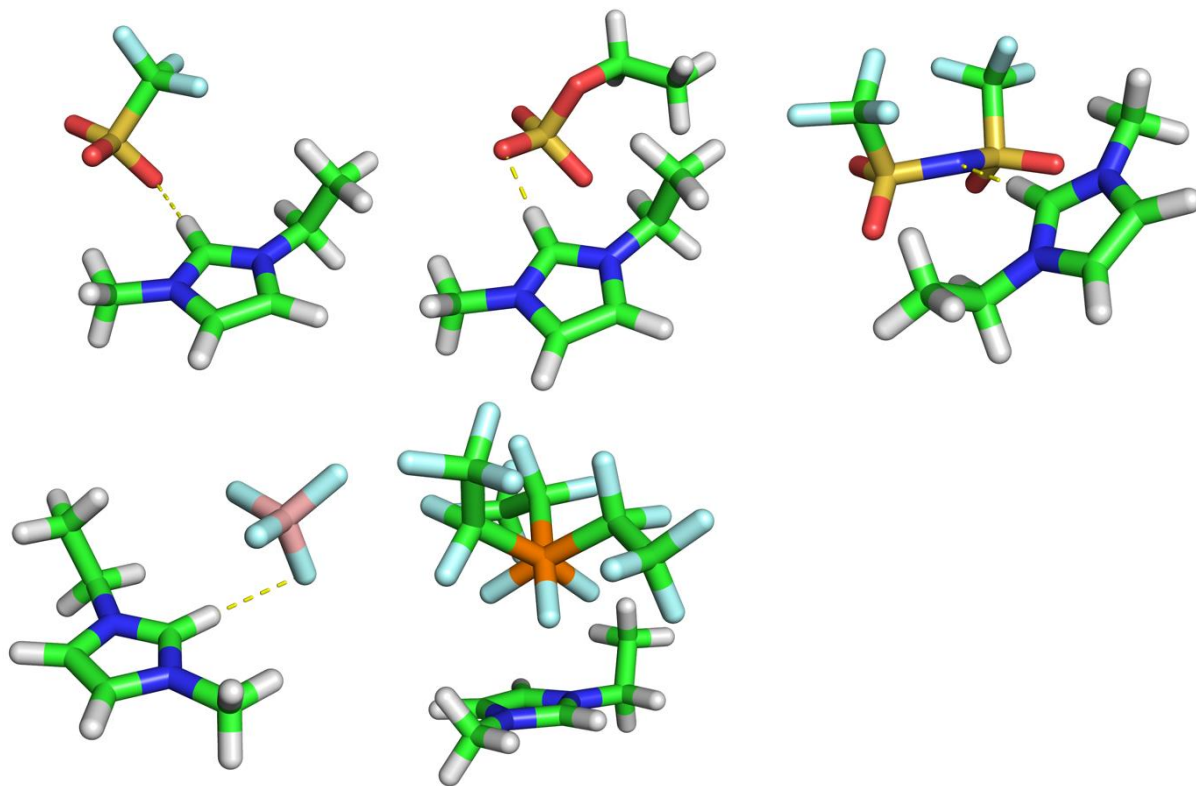


Figure S4(b). Optimized structures (ω -B97XD/def2-TZVP) for complexes of EMIM with EtSO₄, CF₃SO₃, Tf₂N, BF₄, and FAP.

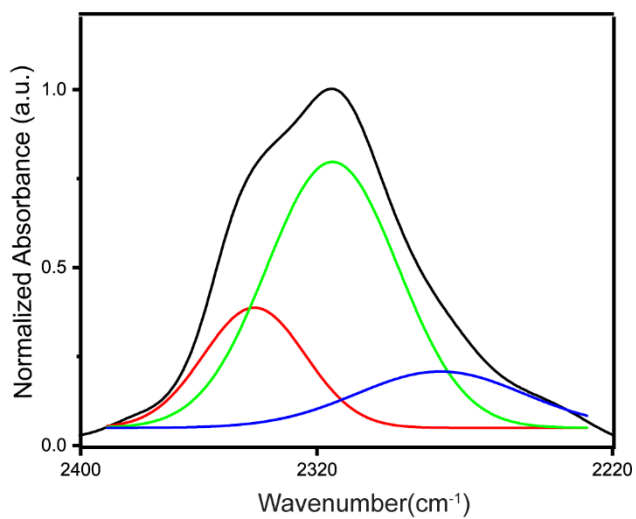


Figure S4(c). Gaussian fitting of the C2-D band of the ionic liquid, [EMIM][EtSO₄], shows multiple peaks.

S5. 2D-IR of N₂O in C2-D labeled [EMIM][FAP].

The dual frequency 2D-IR instrument allowed us to capture the profile of C-D and N₂O band. The C-D feature at T = 300 is shown in Fig. S5 (Left) by exciting and probing the sample with pulses center at ~2360 cm⁻¹. In contrast, the cross-peaks were detected by exciting at N₂O frequency and probing at C-D region. Notice that the cross-peaks appear at early time delays.

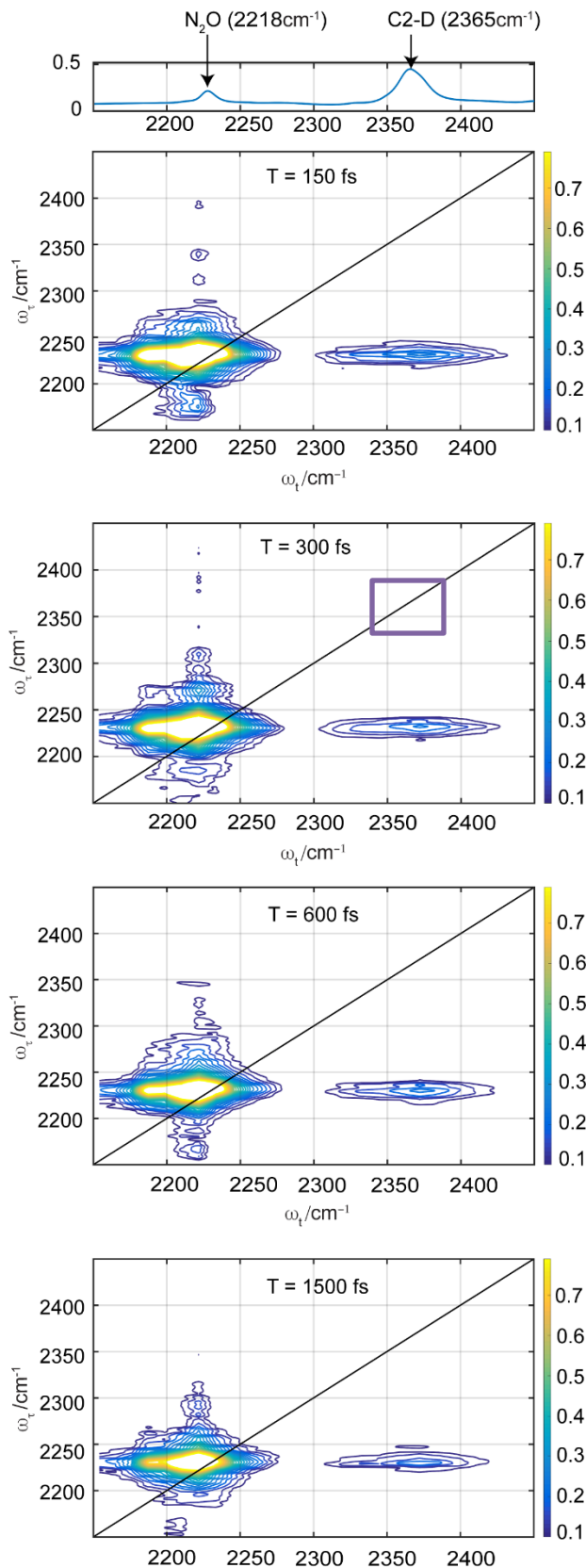
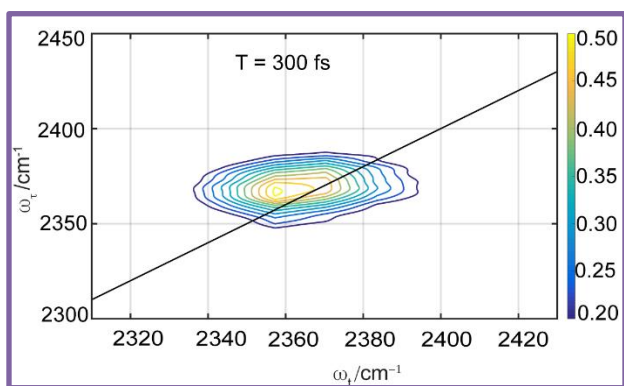


Figure S5. 2D-IR snapshot at different time delays indicates coupling between N₂O in C2-D modes (Right). The C-D profile is highlighted for T= 300 fs (Left).

S6. Analysis of 2D-IR data $^{13}\text{CO}_2$ in C-2D labeled [EMIM][FAP].

$^{13}\text{CO}_2$ was used instead of native $^{12}\text{CO}_2$ to avoid the overlap of the C-2D vibration with the antisymmetric stretch of CO_2 . FT-IR measurements show that $^{13}\text{CO}_2$ has a strong antisymmetric stretch at 2278 cm^{-1} . The 2D-IR spectrum measured at $T = 300\text{ fs}$ (see below) shows a cross peak correlating the $^{13}\text{CO}_2$ asymmetric stretching and C-2D vibration ($\omega_\tau = 2278\text{ cm}^{-1}$, $\omega_t = 2365\text{ cm}^{-1}$). The spectrum was generated by exciting the $^{13}\text{CO}_2$ asymmetric stretch with the first two mid-IR laser pulses centered at 2280 cm^{-1} , and detected by probing the C-2D vibration using a pulse centered at $\sim 2360\text{ cm}^{-1}$. The presence of cross-peak is a significant result as it suggests that the solute CO_2 interacts with the cation even at low concentration.

Unlike N_2O , there are multiple peaks in the region around 2278 cm^{-1} . These features arise from the coupling of the hot band of $^{13}\text{CO}_2$ with the main peak and from other non-linear effects which is in line with the observations made by Fayer² and Garrett-Roe groups³.

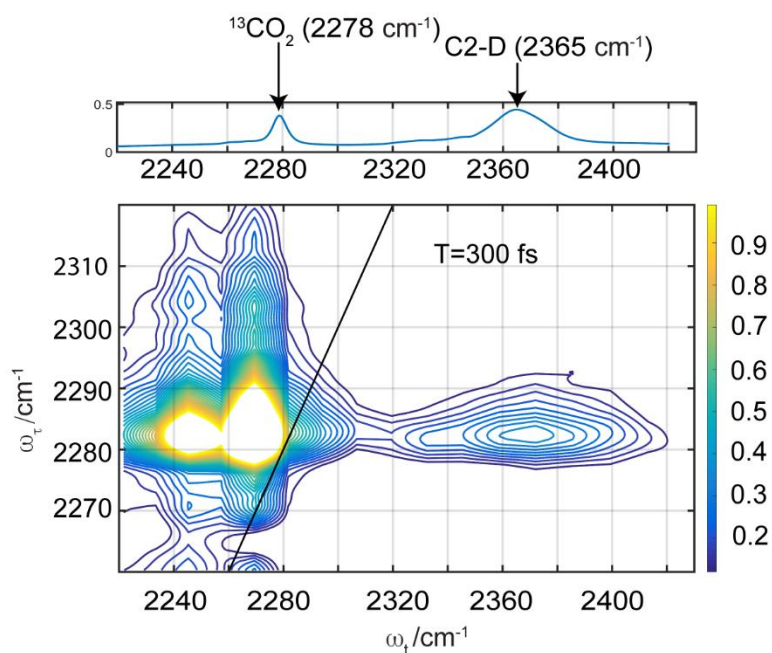


Figure S6. 2D-IR spectra shows that CO_2 interacts with C-2D vibration of [EMIM][FAP]. There is a clear cross-peak at approximately $(2278\text{ cm}^{-1}, 2365\text{ cm}^{-1})$ in the counter plot.

² Giammanco, C. H.; Kramera, Patrick L.; Yamada, Steven A.; Nishida, J.; Tamimi, A.; Fayer, M. D. *J. Chem. Phys.* **2016**, 144, 104506.

³ Brinzer, T.; Berquist, E.; Ren, Z.; Dutta, S.; Johnson, C. A.; Krisher, C. S.; Lambrecht, D. S.; Garrett-Roe, S. *J. Chem Phys.* **2015**, 142(21), 212425.

S7. Estimation of concentration dissolved gases in [EMIM][FAP].

Pure greenhouse gas (N_2O or $^{13}\text{CO}_2$) was dissolved in the liquid ~ 1 atm pressure (See main text for details). To determine the concentration, we used the solubility data of CO_2 at different pressure as reported by Althuluth et al.⁴ It is well known that there is direct relationship between pressure and mole fraction of gas dissolved in ionic liquid at low pressure regimes. Thus, by plotting pressure versus mole fraction for CO_2 from Althuluth et al. work (313.89 K), we were able to determine the following specific equation:

$$Y = 6.8 \text{ Mpa} * X, \text{ where } Y \text{ is the pressure and } X \text{ is the mole fraction}$$

Using this equation, we calculated the mole fraction of CO_2 at 1 atm to be ~ 0.015

For [EMIM][FAP], molar mass and density is known. Using this additional information, the concentration of CO_2 was calculated to be ~ 50 mM

The solubility of N_2O under same condition was assumed to be ~ 5 mM. This is because N_2O is an order less soluble than CO_2 .⁵

Taken together, we can conclude that the solubility of both gases is less 100 mM in the liquid when tested by 2D-IR.

⁴ Althuluth, M.; Mota-Martinez, M.T.; Kroon, M. C.; Peters, C. J. *J. Chem. Eng. Data* **2012**, 57 (12), 3422–3425.

⁵ Chen, Yushu ; Mutelet, Fabrice ; Jaubert, Jean-Noël *Fluid Ph. Equilibria* **2014**, 372, 26–33.