Detailed Overview about Hydrogen-Bonding Motifs in Hydroxy-Functionalized Ionic Liquids

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Formation of Cationic Clusters in Ionic Liquids

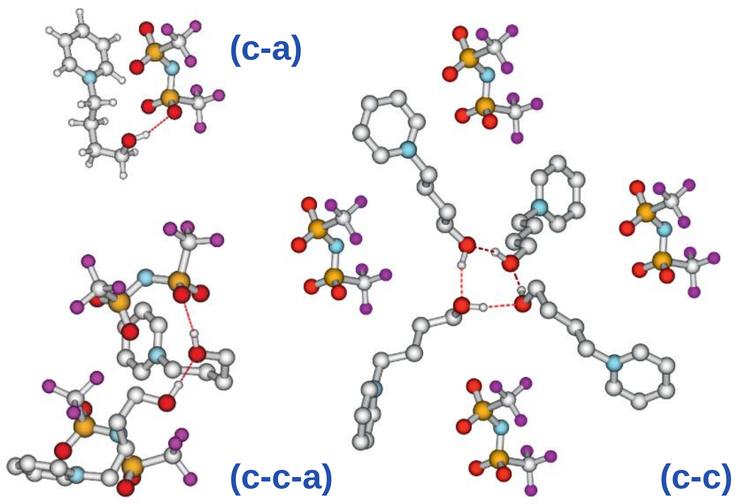

Fig. 1: H-bonded cluster species present in the IL $[HOC_4Py][NTf_2]$: (c-a) describes an H-bond between cation and anion, while (c-c) represents an H-bond between two cations.[1,2]

Criteria for the Formation of c-c Clusters

Cationic hydrogen-bonded clusters in hydroxy-functionalized ILs are formed when (c-a) interactions are weakened and (c-c) hydrogen bonding is favored. This requires:

(i) Weakly Interacting Anions
which avoid binding to cationic OH groups

(ii) Polarizable Cations
that stabilize anion association away from the hydroxyl site

(iii) Increased Alkyl Chain Length
to reduce Coulomb repulsion between cations.

OH-Stretching Region in Mid-IR Spectra

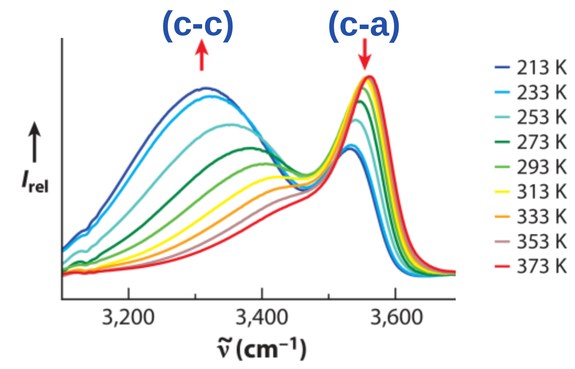

Fig. 2: Infrared spectra of the IL $[HOC_4Py][NTf_2]$: (c-c) vibrational bands show stronger redshifts compared to (c-a) contributions. With decreasing temperature (c-a) decreases to the benefit of (c-c). [1,3]

H-Bond Lifetimes from MD Simulations

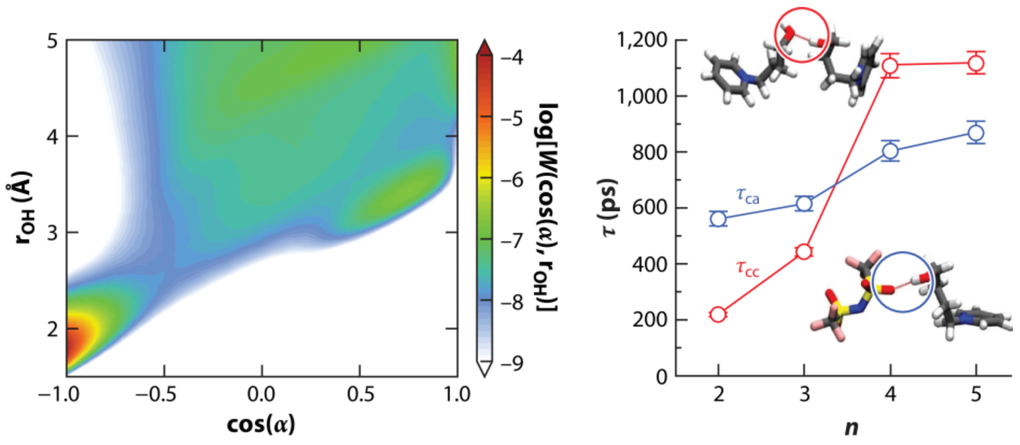

Fig. 3: Left: The (c-c) H-bond geometry is shown as a representation of the r^{-2}-weighted probability density W of finding an intermolecular O-H distance r_{OH} and the cosine of the angle α between the intermolecular H-O vector and the intramolecular O-H vector obtained at 300 K for $[HOC_2Py][NTf_2]$. The (c-c) H-bond can be characterized by a distance cutoff of r_{OH} = 2.7 Å and an angular cutoff at cos(α) = −0.5. For the (c-a) H-bond, the same angular cutoff was used with a distance cutoff of r_{OH} = 2.8 Å. Right: H-bond lifetimes τ for (c-a) (blue) and (c-c) (red) H-bonds as a function of the hydroxyalkyl chain length n at 300 K. For short chains (n = 2, 3), the (c-a) H-bond lifetime is greater than the (c-c) H-bond lifetime. Conversely, for longer chains (n = 4, 5), the (c-c) H-bond is more stable. [1,4]

Influence on Macroscopic Properties

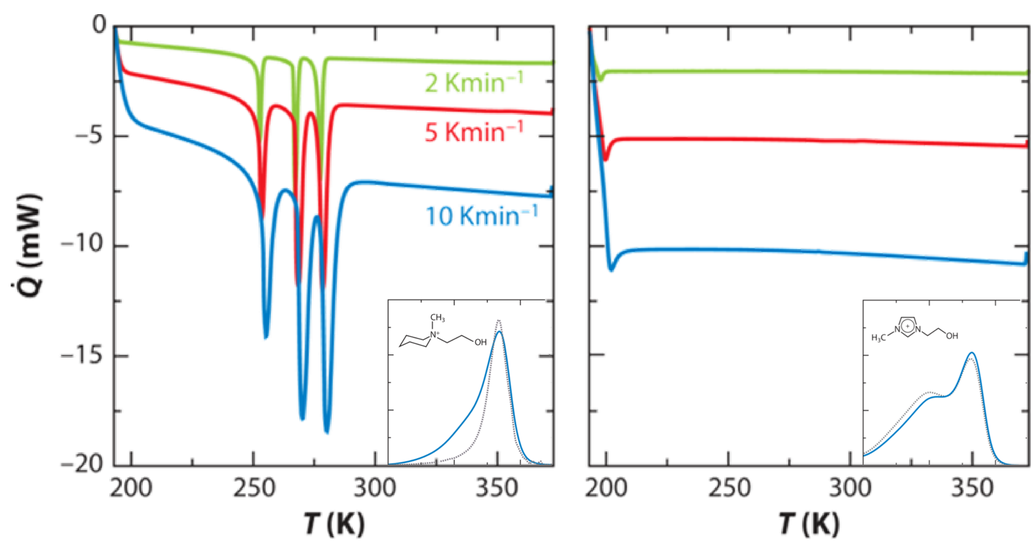

Fig. 4: Differential scanning calorimetry (DSC) thermograms for different heating rates and IR spectra in the O-H stretching region of the ILs $[HOC_2MPip][NTf_2]$ and $[HOC_2MIm][NTf_2]$ for the lowest (253 K, 193 K) and second-lowest (273 K, 213 K) temperatures. The vibrational bands above and below 3,500 cm^{-1} indicate (c-a) and (c-c) hydrogen bonding, respectively. For $[HOC_2MPip][NTf_2]$, the small amount of c-c clusters disappears upon cooling (dashed line), resulting in a symmetric vibrational band indicating pure (c-a) interactions. This behavior is in accordance with the DSC traces, which show phase transitions in this temperature range. For the IL $[HOC_2MIm][NTf_2]$, the number of cationic clusters further increases with decreasing temperature, avoiding crystallization and resulting in a glass transition at about 200 K independent of the heating rate at 2 K min^{-1}, 5 K min^{-1}, or 10 K min^{-1}.

Molecular Level Picture by CIVP Spectroscopy

Pure Ionic Liquids

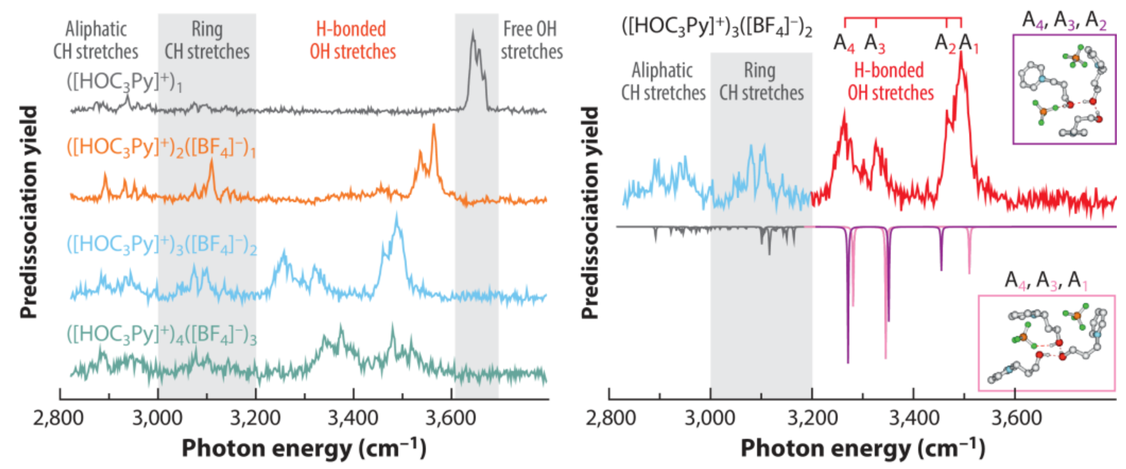

Fig. 5: Left: Photodissociation spectra of N_2-tagged $([HOC_3Py]^+)_1$, $([HOC_3Py]^+)_2([BF_4]^-)_1$, $([HOC_3Py]^+)_3([BF_4]^-)_2$, and $([HOC_3Py]^+)_4([BF_4]^-)_3$. The OH stretches are colored in red. Right: The labels A_1, A_2, A_3, and A_4 denote the H-bonded OH features in the (3,2) cluster. Inverted traces display the calculated spectra for two $([HOC_3Py]^+)_3([BF_4]^-)_2$ isomers shown in the purple and pink boxes. [1,5]

Comparison with Molecular Mimics

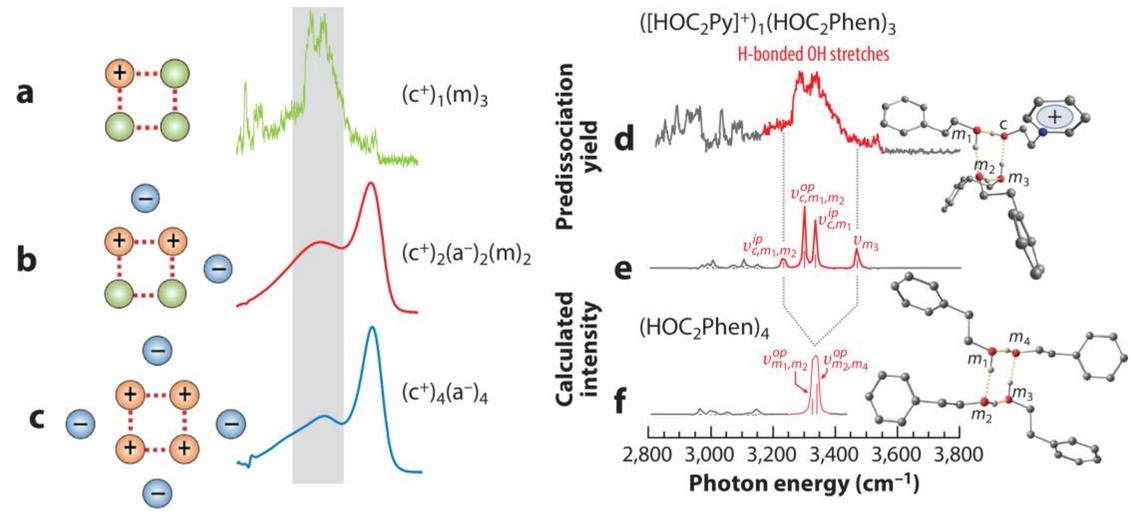

Fig. 6: Possible H-bonded structural motifs explaining the infrared spectra observed in the liquid and gas phases. (a) Positively charged cyclic tetramers $(c^+)_1(m)_3$ in the gas phase. (b) Neutral cyclic tetramers $(c^+)_2(a^-)_2(m)_2$ in the bulk phase, wherein two ion pairs $(c^+)(a^-)$ are replaced by two molecules (m). (c) Neutral cyclic tetramers $(c^+)_4(a^-)_4$ solely consisting of ion pairs in the liquid phase. Vibrational predissociation spectra of (d) N_2-tagged $([HOC_2Py]^+)_1(HOC_2Phen)_3$, compared to (e) its calculated spectrum. (f) Calculated spectrum of the cyclic molecular mimic tetramer $(HOC_2Phen)_4$ is also presented for comparison. [1,6]

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