

## The fate of the proton in protic and aprotic ionic liquids: acidity and ion transfer studied by Raman spectroscopy

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Ionic liquids (ILs), interesting for their tunable solvation behavior and ability to reach high acidities, are commonly classified as protic (PILs) and aprotic (AILs). PILs result from proton transfer between a Brønsted acid and a Brønsted base, yielding a protonated cation. However, acidity is not restricted to PILs, as both PILs and AILs can be acidic depending on whether the proton is associated with the cation or with an acidic anion, respectively.<sup>1</sup> Moreover, high acidity can also be achieved by dissolving Brønsted acids in ILs, owing to the weakly coordinating nature of their anions, leading to high proton activity.

Acidity in ILs is commonly evaluated using Hammett acidity functions, based on the protonation of weakly basic indicators. Protonation is traditionally monitored by UV-Visible spectroscopy, but Raman spectroscopy has been recently implemented in AILs, which allowed us to reveal the influence of the indicator concentration on acidity determination, an effect previously unexplored.<sup>2,3</sup> These results, and the comparison with those obtained with UV-Vis, highlighted the presence of ion pairing in ILs, and how the latter differently influences the UV and Raman spectra, leading to differences in the measured acidity. This hypothesis was further investigated by measuring acidity functions in dissociating and non-dissociating solvents, in which ion pairing is present or minimized.

Raman spectroscopy is also a valuable tool for probing proton transfer in PILs. Studies were performed on a sulfonic acid-functionalized ammonium IL paired with a methanesulfonate anion with and without the presence of methanesulfonic acid. The analysis of Raman specific bands of the IL, coupled with computational modeling using SMD-GIL solvation model, enabled molecular-level insight into the state of the proton. This combined approach revealed that the proton is not permanently localized but can reversibly shuttle between the ammonium group of the cation and the methanesulfonate anion. Furthermore, it allowed us to follow the evolution of the proton environment upon acid addition, highlighting changes in cation–anion interactions and in the hydrogen-bonding network.

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<sup>3</sup>Renzonnet, A.; Eppe, G.; Malherbe, C. *J. Raman Spectrosc.* **2025**, *56*, 827-834.