Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

A DFT and *ab initio* molecular dynamics simulation study of the infrared spectrum of the protic ionic liquid 2-hydroxyethylammonium formate

Vitor Hugo Paschoal and Mauro C. C. Ribeiro*

Laboratório de Espectroscopia Molecular, Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, 05513-970 São Paulo, SP, Brazil

* corresponding author, email: mccribei@iq.usp.br

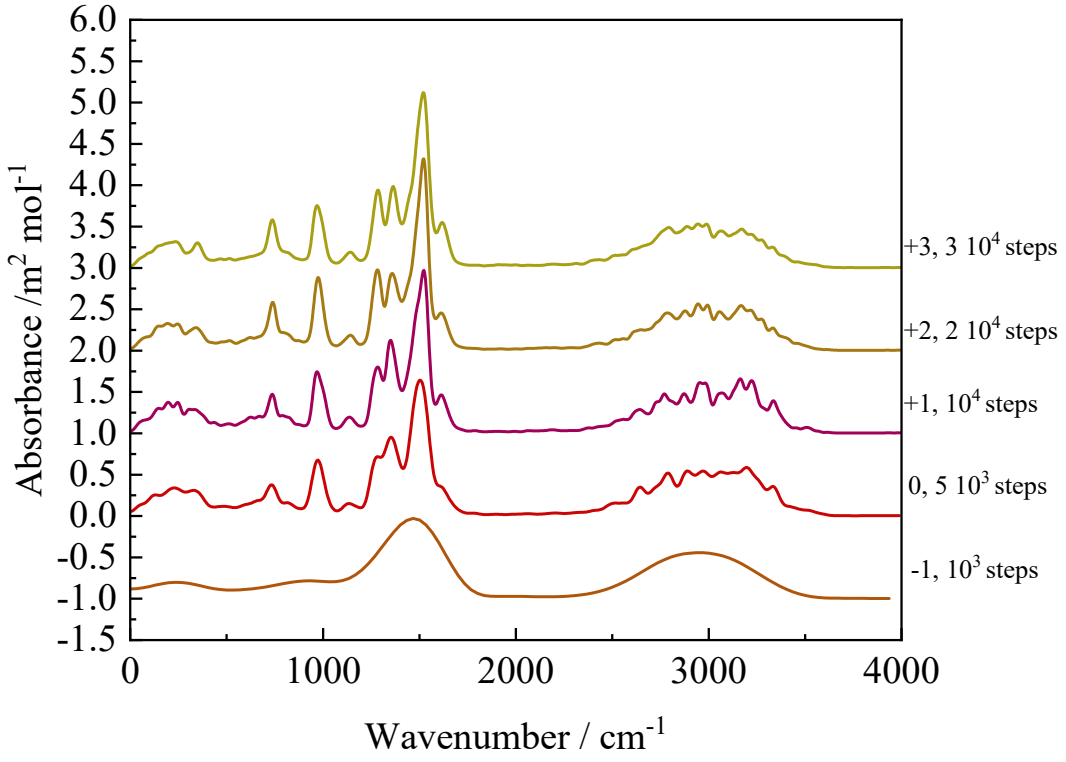

Figure S1. Calculated IR spectra from the AIMD trajectory considering different lengths, ranging from 10^3 steps (brown line, shifted by -1 units of absorbance) to the whole trajectory, 3×10^4 steps (gold line, shifted by three units of absorbance). The spectra are shifted vertically for better visualization.

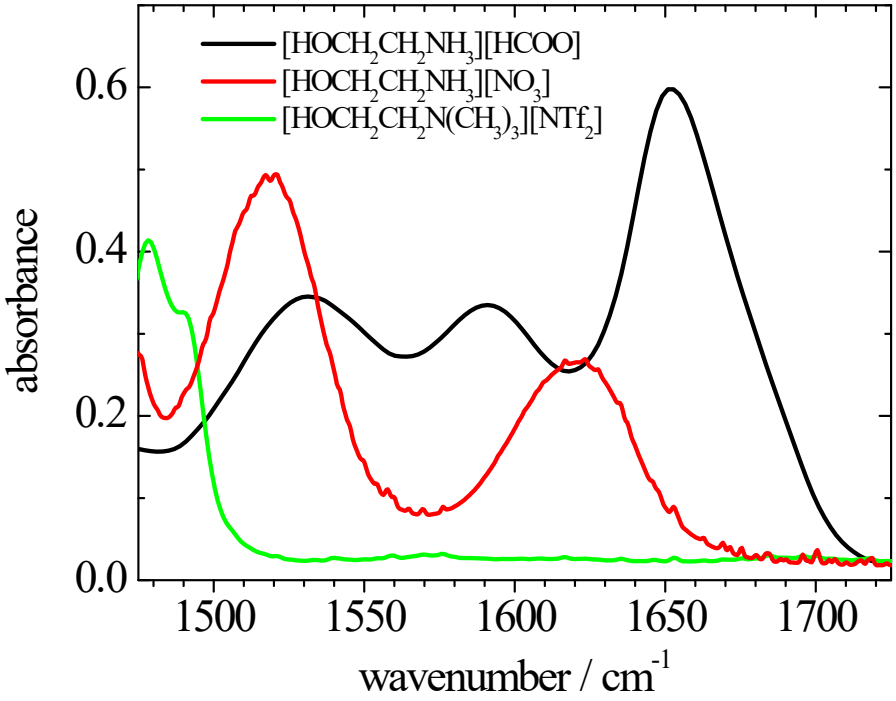

Figure S2. The 1500 – 1700 cm^{-1} range of the infrared spectrum of the PIL under investigation, $[HOCH_2CH_2NH_3][HCOO]$ (black line), compared with the spectra of 2-hydroxyethylammonium nitrate, $[HOCH_2CH_2NH_3][NO_3]$ (red line), and choline bis(trifluoromethanesulfonyl)imide, $[HOCH_2CH_2(NH_3)_3][NTf_2]$ (green line).

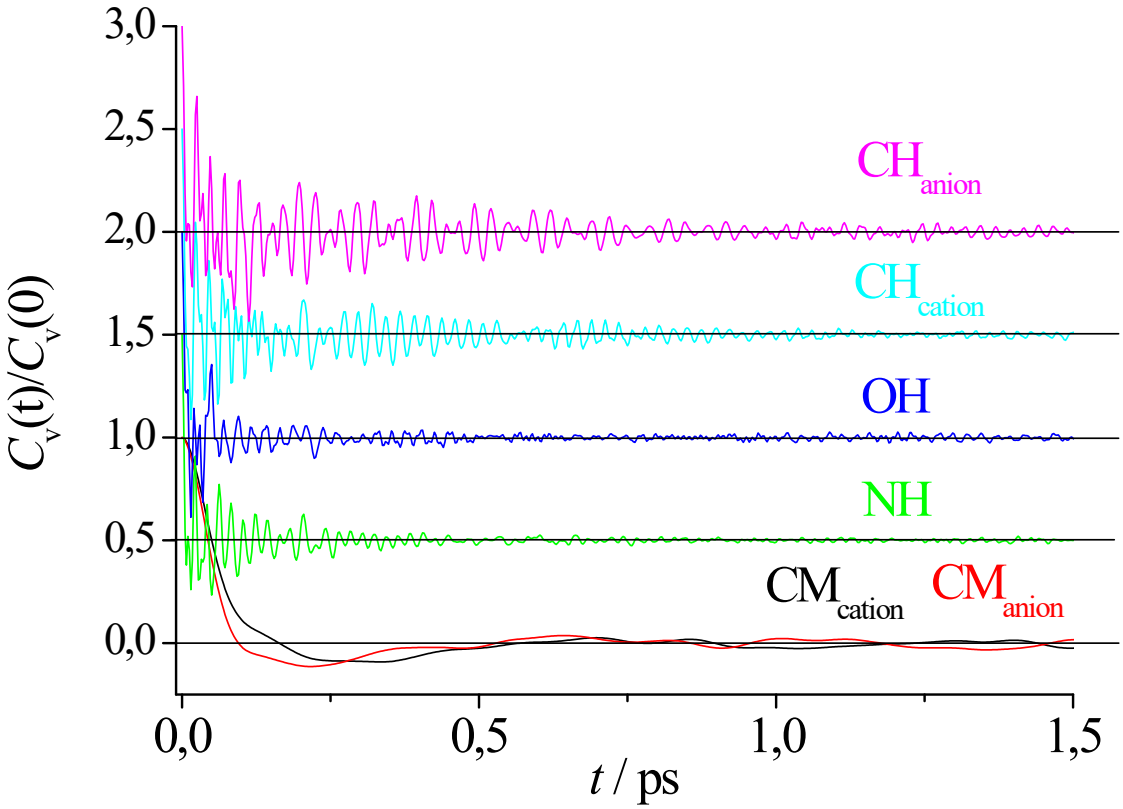

Figure S3. Single-particle time correlation functions of velocities, $C_v(t) = \langle \mathbf{v}_i(0).\mathbf{v}_i(t) \rangle$, calculated by the AIMD simulation of $[HOCH_2CH_2NH_3][HCOO]$. The functions were normalized by its initial value, $C_v(0)$, and the upper four functions were vertically shifted by 0.5 to help visualization. The black and red colored $C_v(t)$ at the bottom correspond, respectively, to the cation and anion center-of-mass velocity. The others $C_v(t)$ correspond to velocities of selected atoms as indicated in the figure: N and H atoms of the cation NH_3 group (green line), O and H atoms of the cation OH group (blue line), C and H atoms of the cation CH_2 groups (cyan line), and C and H atoms of the anion (magenta line).

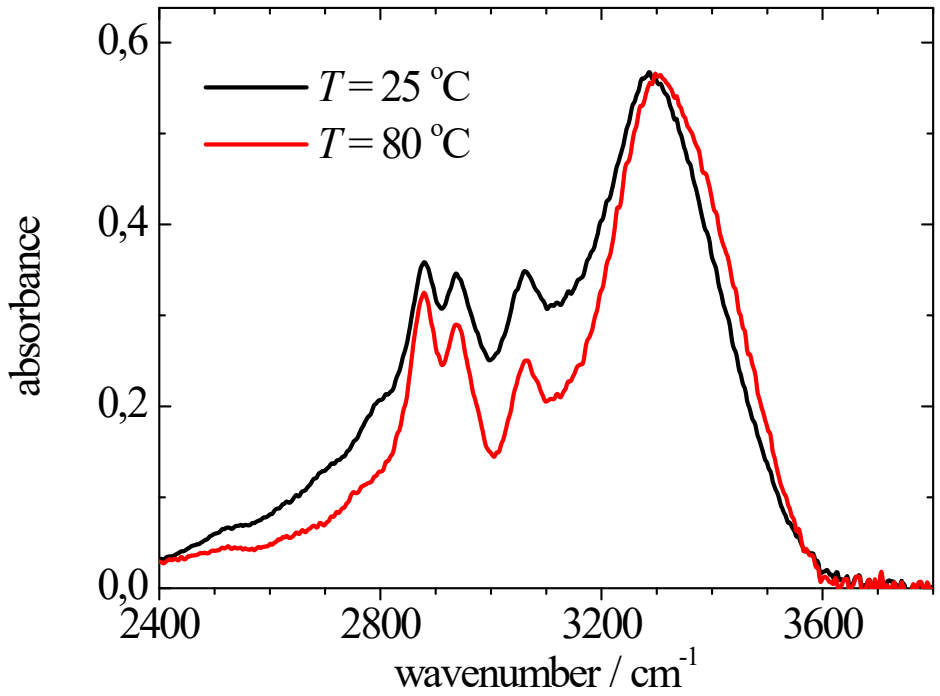

Figure S4. Infrared spectra of $[HOCH_2CH_2NH_3][HCOO]$ at 25 °C (black line) and 80 °C (red line). The intensities have been normalized by the highest intensity peak.

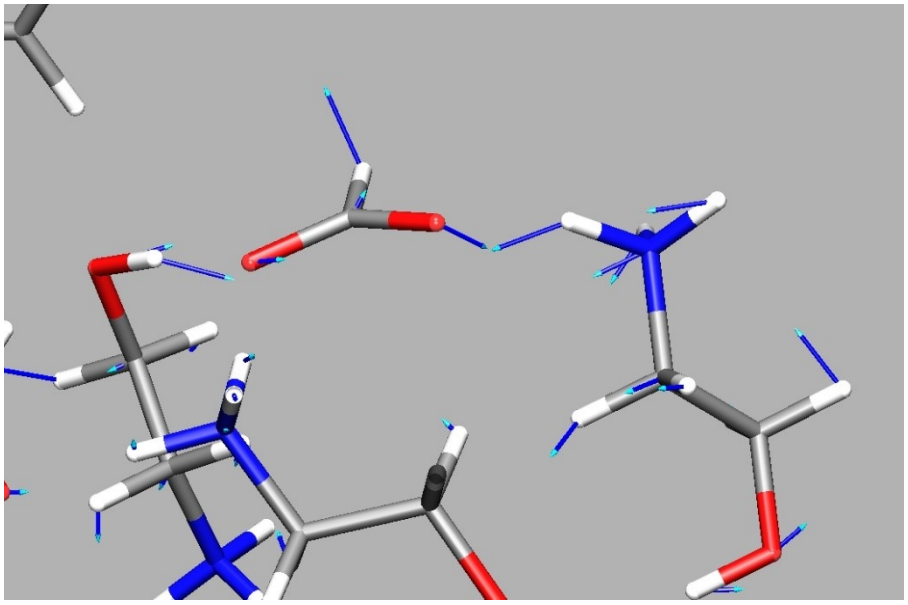

Figure S5. Atomic displacements of the normal mode calculated by DFT at 217 cm^{-1}. The image only emphasizes a portion of the four-ionic pair cluster in order to facilitate better viewing.