Supporting Information for

Exploring asymmetry induced entropy in tetraalkylammonium-urea DES systems: what can be learned from inelastic neutron scattering?

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Contents:

INS spectroscopy in a nutshell

INS spectroscopy provides a unique assessment of the structural dynamics of hydrogenous materials that is not amenable from its optical counterparts, infrared and Raman spectroscopies, as it is not constrained by symmetry-related selection rules. In this way, all the vibrational modes are active in INS (however, it should be mentioned that they can be either weak or fall in an overcrowded region, thus preventing their clear observation in the experimental spectrum).

In INS, the intensity of each fundamental vibrational transition is expressed, for a given atom, by the dynamic structure factor

$$S_i^*(Q, nv_k) \propto \frac{(QU_i)^{2n}}{n!} . \sigma . exp(-Q^2 \alpha_i^2)$$

where Q (Å^{-1}) is the momentum transferred to the sample, n is the quanta involved ($n = 1$ for fundamental modes), v_k is the energy of a vibrational mode, U_i (Å) is the displacement vector of atom i in mode k, σ is the neutron scattering cross section of atom i and α_i (Å) is related to a mass-weighted sum of the displacements of the atom in all vibrational modes, a term whose magnitude is in part determined by the thermal motion of the molecule. This means that the intensity of a band associated with a given vibrational mode is proportional to neutron scattering cross section of the moving nuclei and to the amplitude of nuclei displacement. While the former is a physical property of the nuclei, the latter is readily obtained from periodic-DFT calculations (frequency, or phonon, calculations).

The variable Q, the momentum transferred to the sample, accounts for the fact that neutrons possess mass and thus any scattering event may involve a change in both energy and momentum. This dependence on Q is what makes INS spectroscopy different from its optical counterparts. Neutrons probe the entire Brillouin zone (different k-vector and momentum transfer), while infrared and Raman are limited to the zone center (Γ-point, $Q=0$).

Equation above also contains an exponential term known as the Debye-Waller factor, which is partially determined by the thermal motion of the sample. By cooling the sample, this thermal motion can be reduced, leading to better results; for this reason, neutron spectra are usually obtained at temperatures below 20 K. Hence, the use of INS spectroscopy to study DES assumes that it is possible, to a large extent, to preserve the room-temperature morphology of the liquid phase at these low temperatures. To this end, samples are usually quenched in liquid nitrogen ("shock frozen"), at ca. 77 K, prior to placement inside the cryostat in which the spectrum is collected. The sudden temperature drop, combined with the high viscosity of DES, is expected to prevent crystallization or phase separation in the sample at low temperature and preserve a liquid-like organization. This effect has been confirmed experimentally, when comparing the effect of "shock freeze" and "slow cooling" of the cholinium chloride: urea DES.

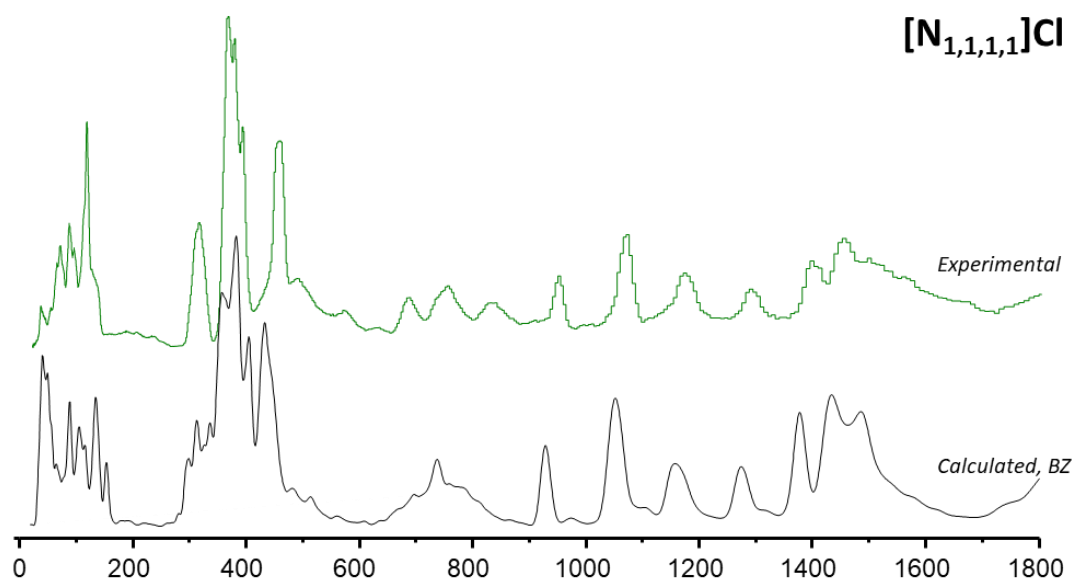## A) The pure compounds: calculated vs. experimental spectra

Figure 1S – Experimental (top line, red) and calculated (middle, bottom) spectra for tetramethylammonium cholride, [N₁,₁,₁,₁]Cl . Calculated spectrum includes dispersion over the Brillouin zone and multiquanta transitions.
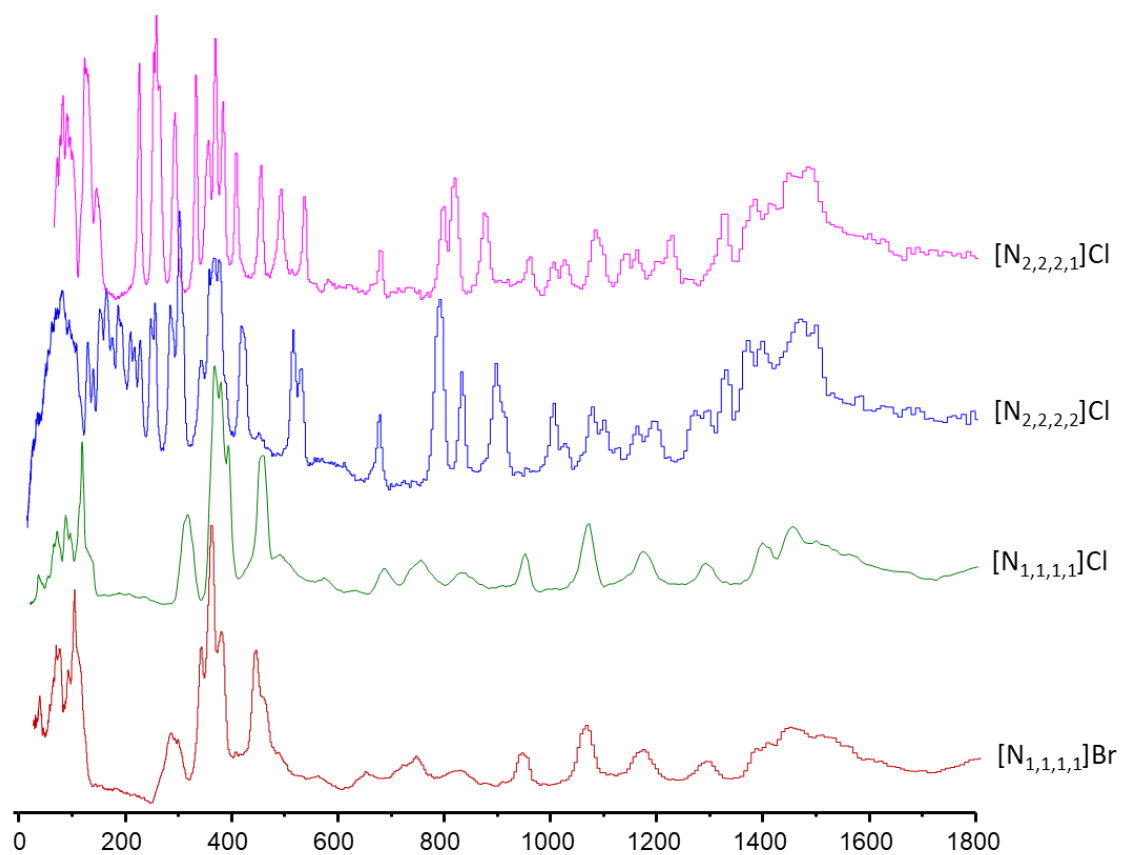

Figure 2S – Comparison of the experimental INS spectra for the four salts.

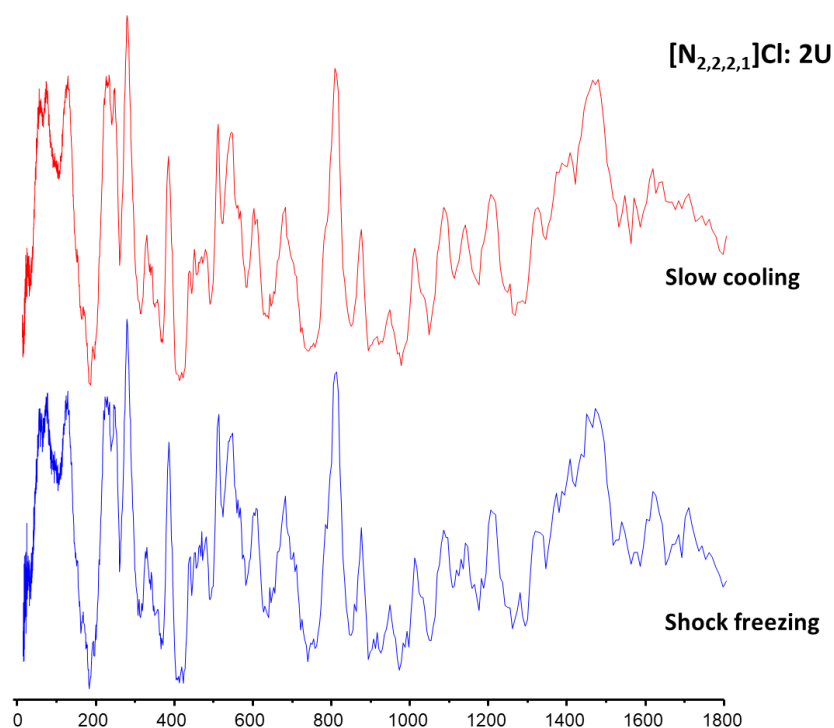## B) The INS spectra of alkylammonium:urea mixtures

[N$_{2,2,2,1}$]Cl: 2U

Slow cooling

Shock freezing

Figure 3S – Example of "shock freezing" versus "slow cooling" of DES mixtures: the case of the [N2,2,2,1]Cl:Urea mixture.

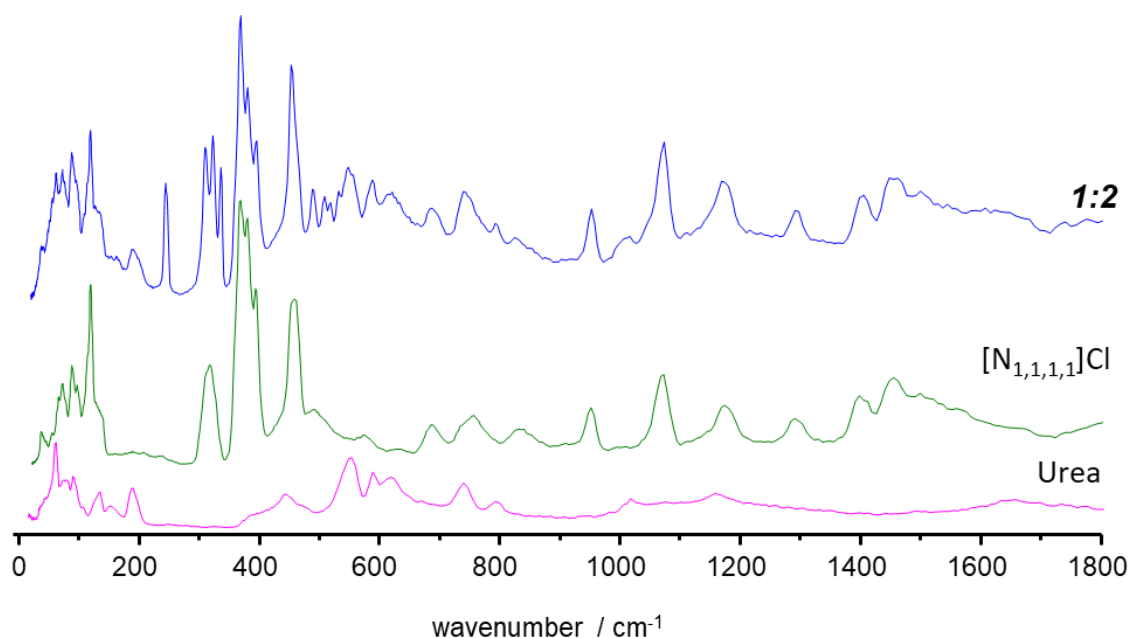*1:2*

[N$_{1,1,1,1}$]Cl

Urea

wavenumber / cm^{-1}

Figure 4S – INS spectrum of the tetramethylammonium chloride:urea 1:2 mixture (top line, green), compared with the INS spectrum of pure components, urea (bottom, magenta) and tetraethylammonium chloride (middle, blue).
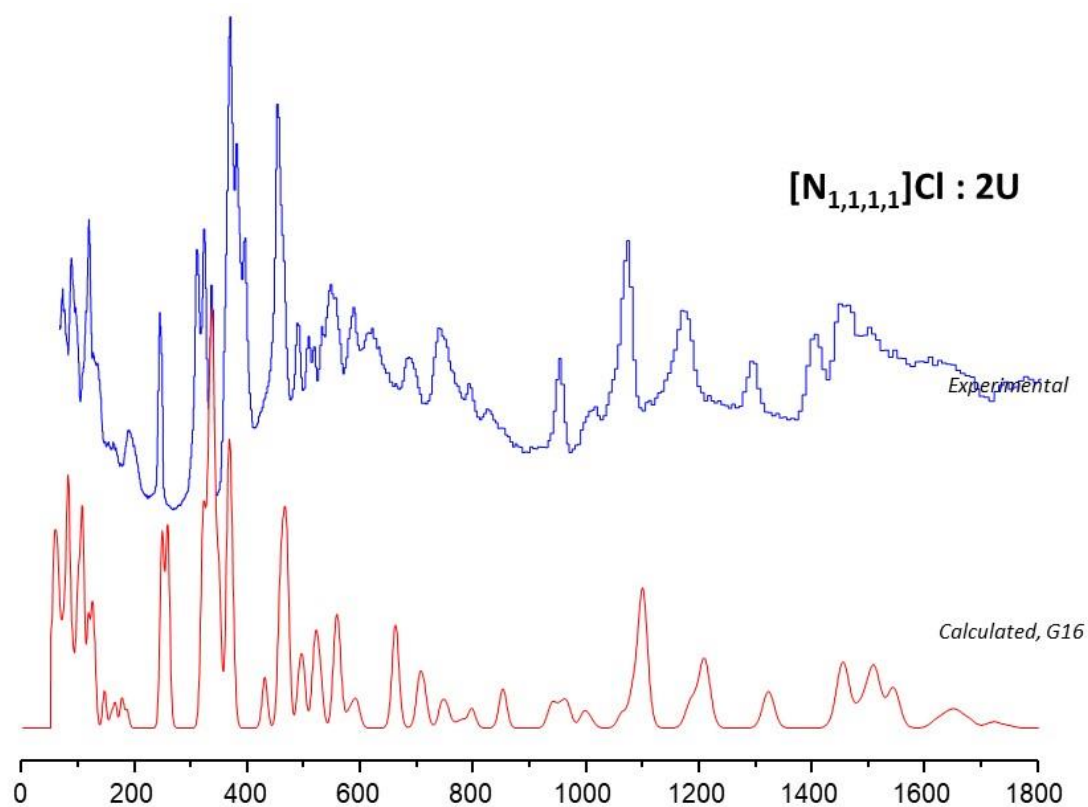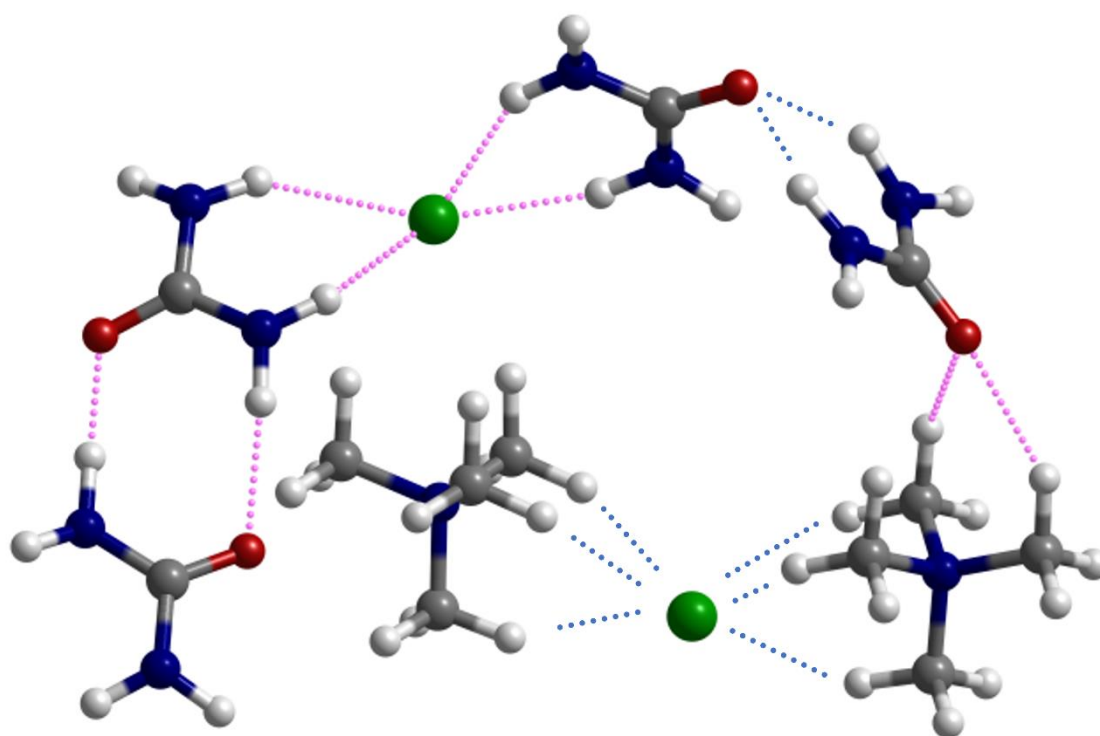
Figure 5S *– Optimized geometry for the (tetramethylammonium chloride:urea 1:2)x2 cluster and comparison between experimental (top line) and calculated spectra based on the above cluster (bottom line). Short intermolecular contacts in the cluster are highlighted.*
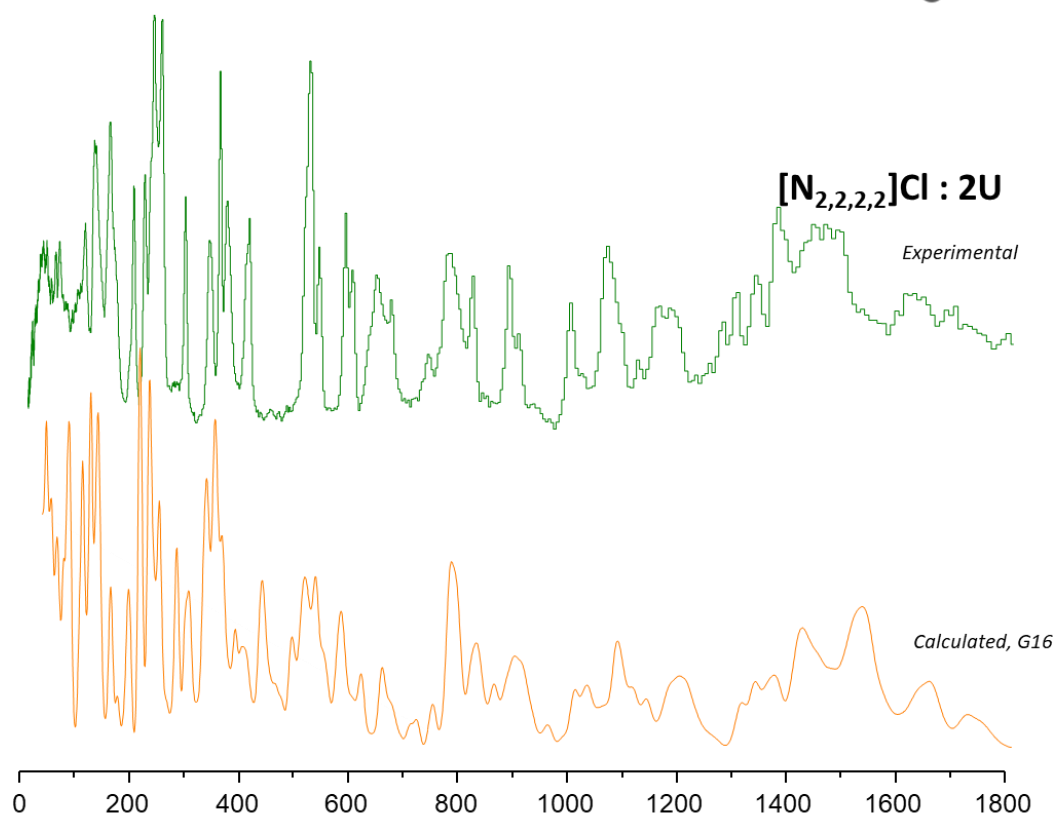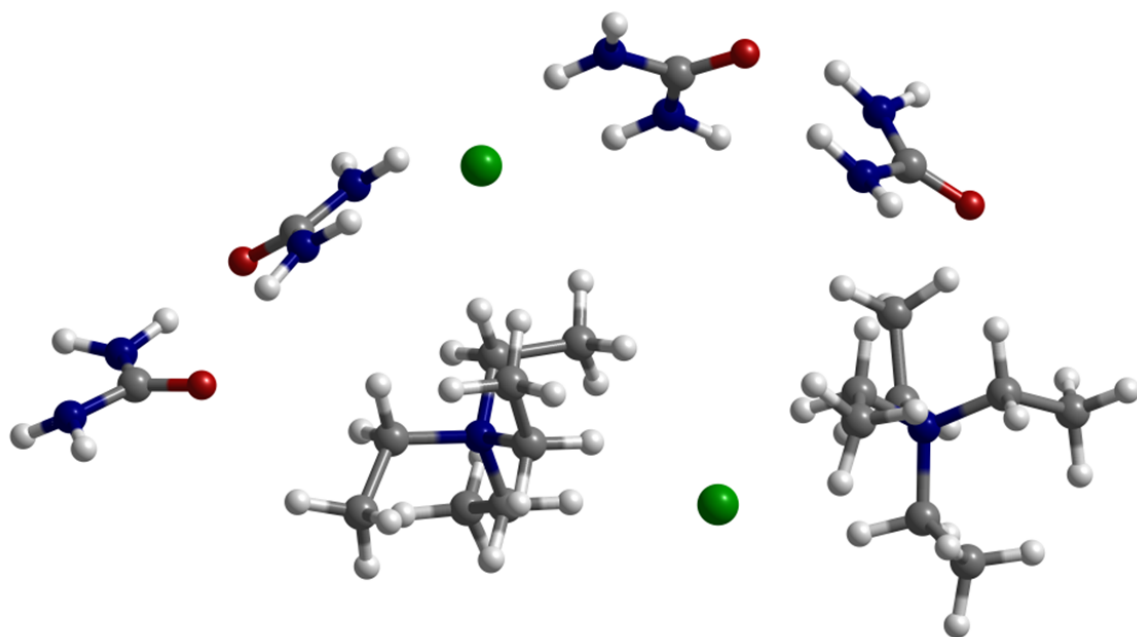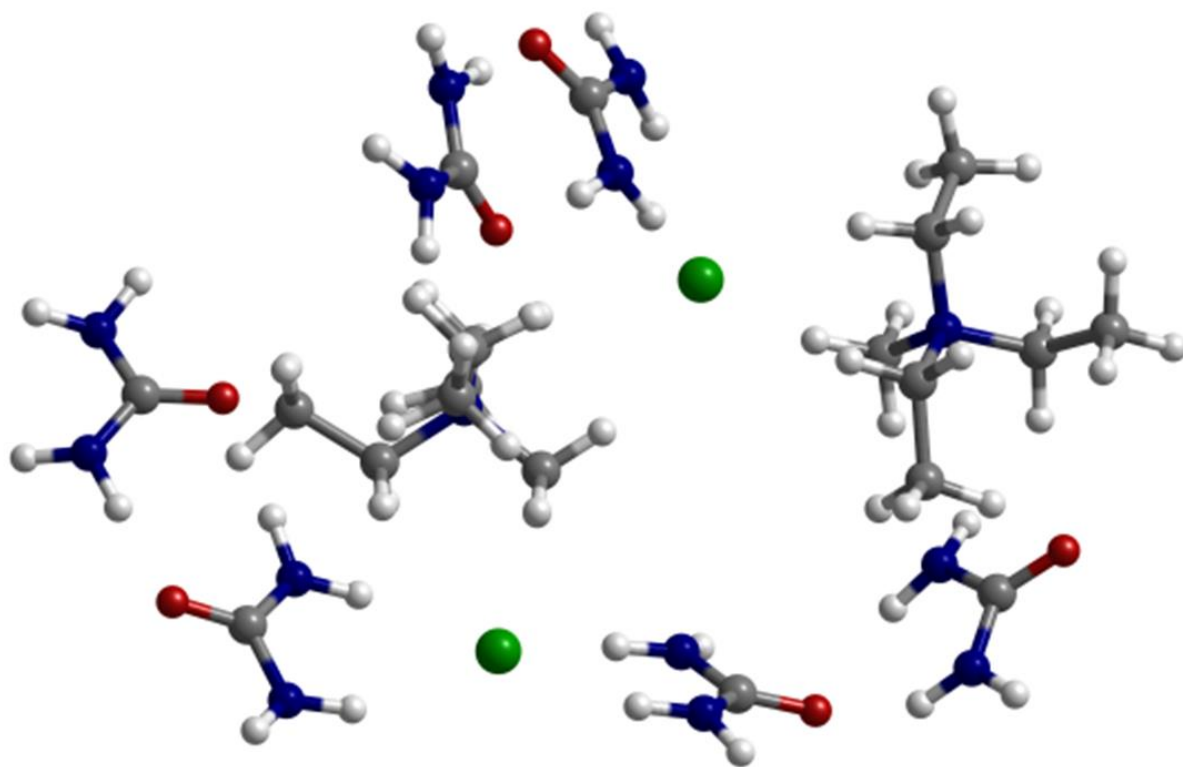
Figure 6S – *Optimized geometry for the (tetraethylammonium chloride:urea 1:2)x2 cluster and comparison between experimental (top line) and calculated spectra based on the above cluster (bottom line).*

[N₂,₂,₂,₁]Cl : 3U

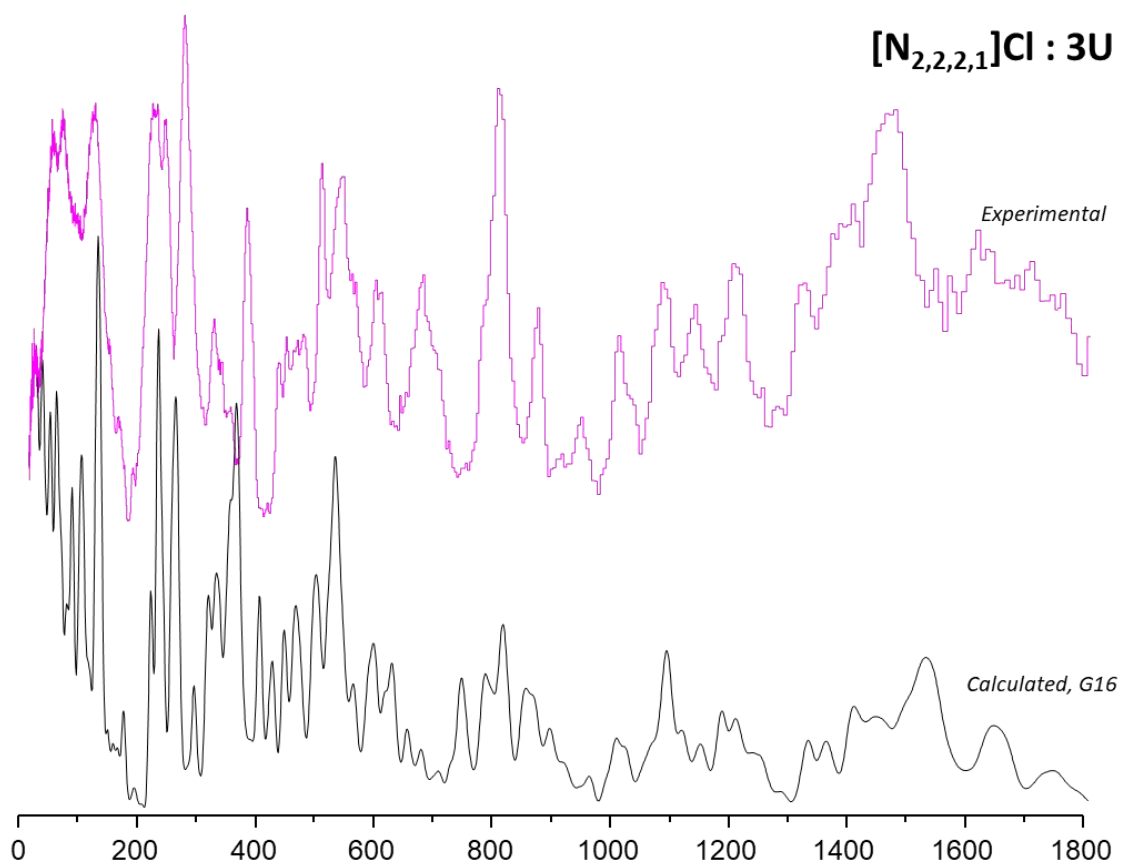*Experimental*

Calculated, G16

Figure 7S *– Optimized geometry for the (triethylmethylammonium chloride:urea 1:3)x2 cluster and comparison between experimental (top line) and calculated spectra based on the above cluster (bottom line).*
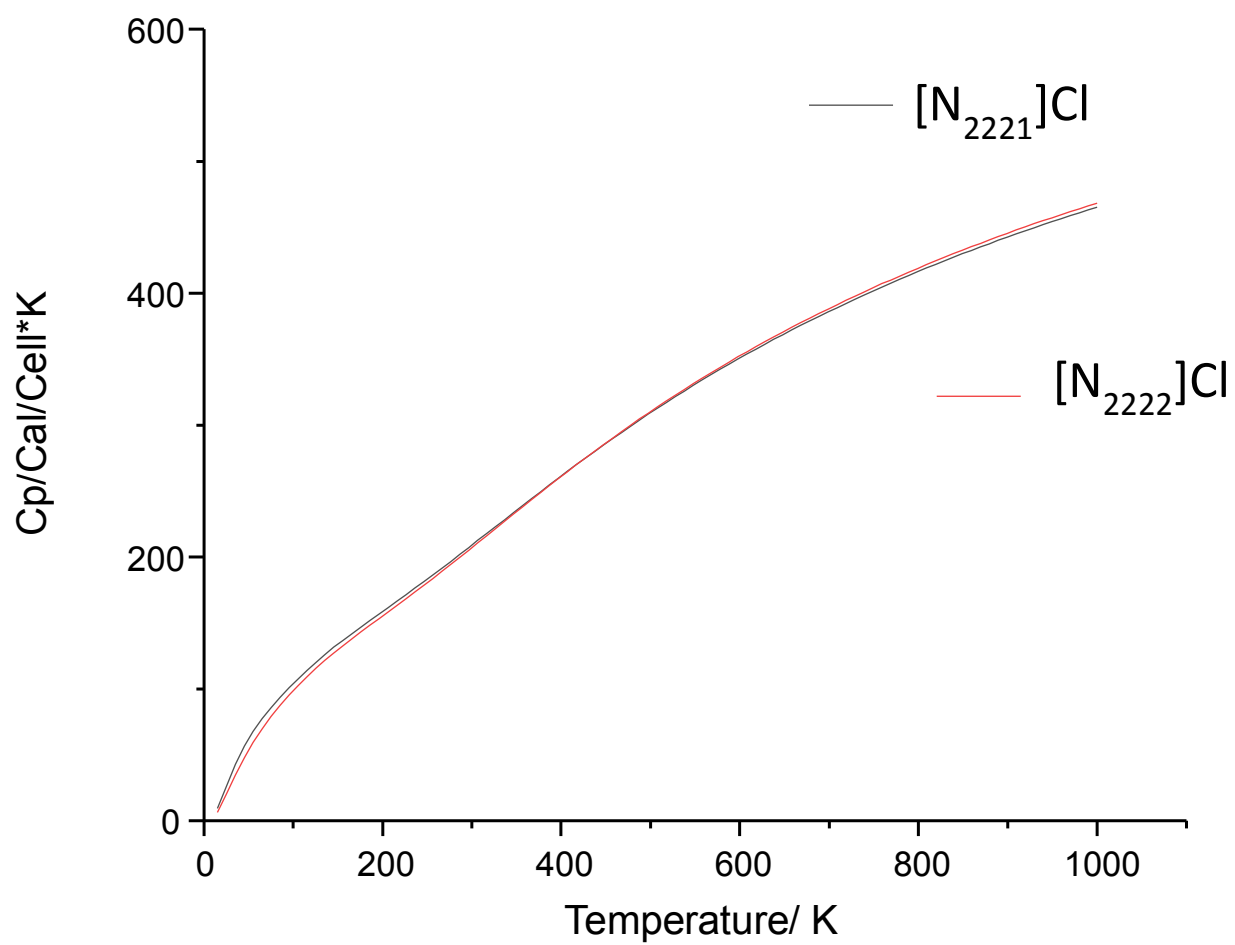
Figure 8S *– Temperature dependence of heat capacity for [N$_{2,2,2,2}$]Cl and [N$_{2,2,2,1}$]Cl obtained from periodic DFT calculations.*