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

Inelastic Neutron Scattering study of Reline:

shedding light on the hydrogen bonding network of deep eutectic solvents

Supporting Material

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Figure S1. Optimized geometry of the aggregate used to model Reline, with dotted lines evidencing hydrogen bonding sites. This image was rendered using the ChemCraft program (http://www.chemcraftprog.com).

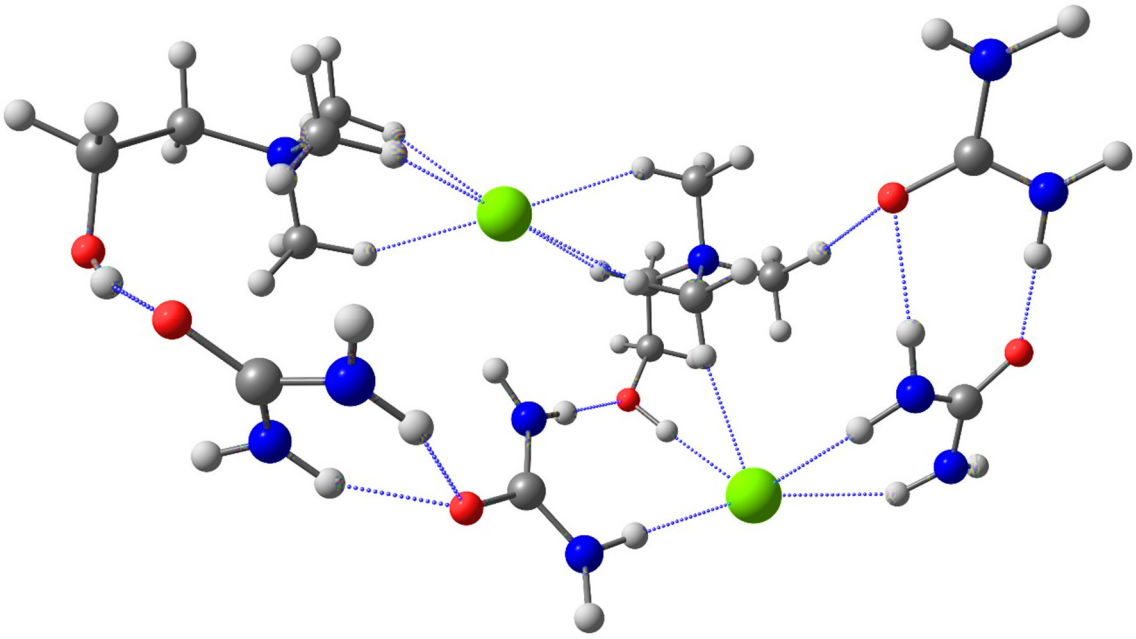

Table S1. Coordinates of reline's model optimized geometry

N	2.261656000	-1.120176000	1.554849000
C	1.884686000	-2.570277000	1.381075000
H	0.795557000	-2.631545000	1.318832000
H	2.354022000	-2.929988000	0.464392000
H	2.254961000	-3.133264000	2.240184000
C	1.782484000	-0.375613000	0.326072000
H	0.695970000	-0.461676000	0.288043000
H	2.094478000	0.664398000	0.398277000
H	2.244938000	-0.853027000	-0.538266000
C	3.757755000	-1.008761000	1.654905000
H	4.039325000	0.043510000	1.663160000
H	4.084301000	-1.502591000	2.572665000
H	4.191252000	-1.493624000	0.779641000
C	1.572938000	-0.617532000	2.823958000
C	1.937739000	0.779489000	3.329107000
H	1.838213000	-1.342620000	3.600849000
H	0.498739000	-0.691857000	2.626709000
H	1.498365000	0.832744000	4.335020000
H	3.021125000	0.896548000	3.453251000
O	1.405899000	1.835013000	2.558679000
H	2.129833000	2.286899000	2.053083000
Cl	3.421576000	3.016832000	0.643392000
C	6.243184000	0.805734000	-0.758686000
O	7.062892000	-0.133275000	-0.859430000
N	4.979846000	0.738012000	-1.268544000
H	4.635185000	-0.190376000	-1.491425000

H	4.303894000	1.438336000	-0.970757000
N	6.583449000	1.990368000	-0.167703000
H	7.471797000	2.005583000	0.307728000
H	5.851532000	2.620825000	0.149406000
C	5.021727000	-2.944975000	-1.944157000
O	4.135155000	-2.239474000	-1.422049000
N	4.692266000	-4.164161000	-2.514733000
H	3.706577000	-4.279897000	-2.699431000
H	5.310530000	-4.575694000	-3.199152000
N	6.326711000	-2.600434000	-1.944599000
H	6.615429000	-1.691375000	-1.538881000
H	7.027562000	-3.193988000	-2.359306000
N	-5.377316000	-1.744640000	0.679953000
C	-5.069964000	-0.386299000	1.276096000
C	-4.594471000	-1.916891000	-0.599944000
C	-4.912416000	-2.790485000	1.662951000
C	-6.873328000	-1.922510000	0.450519000
C	-7.503516000	-1.171665000	-0.728148000
O	-7.471576000	0.227514000	-0.594277000
H	-5.610560000	-0.304522000	2.220496000
H	-5.410547000	0.383029000	0.590441000
H	-3.990923000	-0.339928000	1.439295000
H	-3.533050000	-1.867788000	-0.341045000
H	-4.847054000	-2.890306000	-1.026170000
H	-4.859636000	-1.117384000	-1.291255000
H	-3.847382000	-2.624502000	1.850713000
H	-5.076916000	-3.777841000	1.228019000
H	-5.492117000	-2.685790000	2.581793000
H	-7.357073000	-1.623749000	1.384321000
H	-7.032036000	-2.995940000	0.303723000
H	-7.053599000	-1.492986000	-1.675220000
H	-8.549894000	-1.511721000	-0.744747000
H	-6.852855000	0.592652000	-1.276847000
Cl	-1.643071000	-1.393876000	1.291338000
C	-0.785317000	3.036077000	-0.409125000
N	-0.784729000	2.094931000	0.565018000
H	-1.461782000	1.344859000	0.532135000
H	-0.062117000	2.036145000	1.278743000
N	0.252862000	3.920205000	-0.418688000
H	0.271973000	4.541579000	-1.212757000
H	1.153285000	3.701912000	0.006692000
O	-1.713879000	3.126557000	-1.253496000
C	-4.540881000	1.545218000	-2.087123000
N	-4.522179000	2.503550000	-1.118465000
H	-5.407595000	2.870598000	-0.808627000
H	-3.663673000	3.034895000	-0.970730000
N	-3.362214000	1.318762000	-2.713060000
H	-3.324108000	0.582931000	-3.398165000
H	-2.529147000	1.836394000	-2.433402000
O	-5.573183000	0.880652000	-2.357557000

Table S2. Assignment of reline's vibrational modes. The first three columns list the vibrational frequency in cm-1.

Coline Chloride	***Urea***	***Reline***	***Obs.***	***Technique***
50	62	48	*Lattice mode*	INS
64	74		*Lattice mode*	INS
77	80	72	*Lattice mode*	INS
84	90		*Lattice mode*	INS
112	107		*Lattice mode*	INS
	126		*Lattice mode*	INS
123	135		*Lattice mode*	INS
139	152		*Lattice mode*	INS
	188	178?	*Lattice mode*	INS
211		178?	τCC + νOH…Cl/ν OH…O=C	INS
279		shldr	δNCC	INS
286		252	τCH_3	INS
321		shlδr	$\rho N(CH_3)_3$	INS
341		296	Mainly $(\tau CH_3)_{Ch}$ small cont of $(\omega_{as}NH_2)_U$	INS
349		333	τCH_3	INS
371		373	$\rho N(CH_3)_3$	INS
421		421	$\delta N(CH_3)_3$	INS
447, 466	443	448	$(\delta N(CH_3)_3)_{Ch}$ small cont of $(\omega_s NH_2)_U$	INS
532	546	526	$(\delta NCN)_U$, small cont of $(\delta NCC/CCO)_{Ch}$	Raman
	588, 618	587	$\tau_{as}NH_2$ small cont of δCO	INS
623		?	τOH	INS
719		714	ν_s(1) CN (Ch *gauche*)	Raman
		769	ν_s(1) CN (Ch *trans*)	Raman
	787	787	πCO	FTIR
864		866	ν_s (2) CN	Raman
895		884 shldr	ρCH_2	Raman
953, 960		958	ν_{as} (3,4) CN	Raman
	1010	997	ν_sCN	Raman
1016	1017	1002	$\rho_{as}NH_2$, ρCH_3, ρCH_2, δCOH	INS
1060, 1081		1066	ρCH_3, ρCH_2, δCOH + νCC	INS
1151	1158	1140	$(\rho_s NH_2)_U + (\rho CH_3 + \nu CO)_{Ch}$	INS
1217		1205	ρCH_3	INS
1285		1279	ρCH_3	INS
1344		1344	ωCH_2 + δCOH	INS
1413, 1423		1418	$\delta_s CH_3$ + δCOH	Raman
	1460	1433	ν_{as}CN	FTIR
1451, 1458		1448	δs CH_3 + + δCH_2	Raman
1487		1478	δas CH_3 + δ CH_2	Raman
	1676	1606	**$\underline{\delta NH_2}$** + νC=O	FTIR
	1591	1660	**$\underline{\nu C=O}$** + δNH_2	FTIR
2888		2881	ν_sCH2	Raman
2924		2929	ν_{as}CH2 + ν_sCH3	Raman
2966		2970	ν_{as}CH2 + ν_sCH3	Raman
3025, 3013		3024	ν_{as} CH3	Raman
3219		?	νOH	FTIR
	3256		δ NH_2 + νCO Fermi w/ νNH	FTIR
		3188	? (see discussion)	FTIR
	3333	3315	$\nu_s NH_2$	FTIR
	3427	3417	$\nu_{as}NH_2$	FTIR

τ – torsion; ν – stretching; δ – deformation; ρ – rocking; ω – wagging; π – out-of-plane deformation.

Figure S2. INS spectra of Reline, urea and choline chloride (ChCl) collected using TOSCA

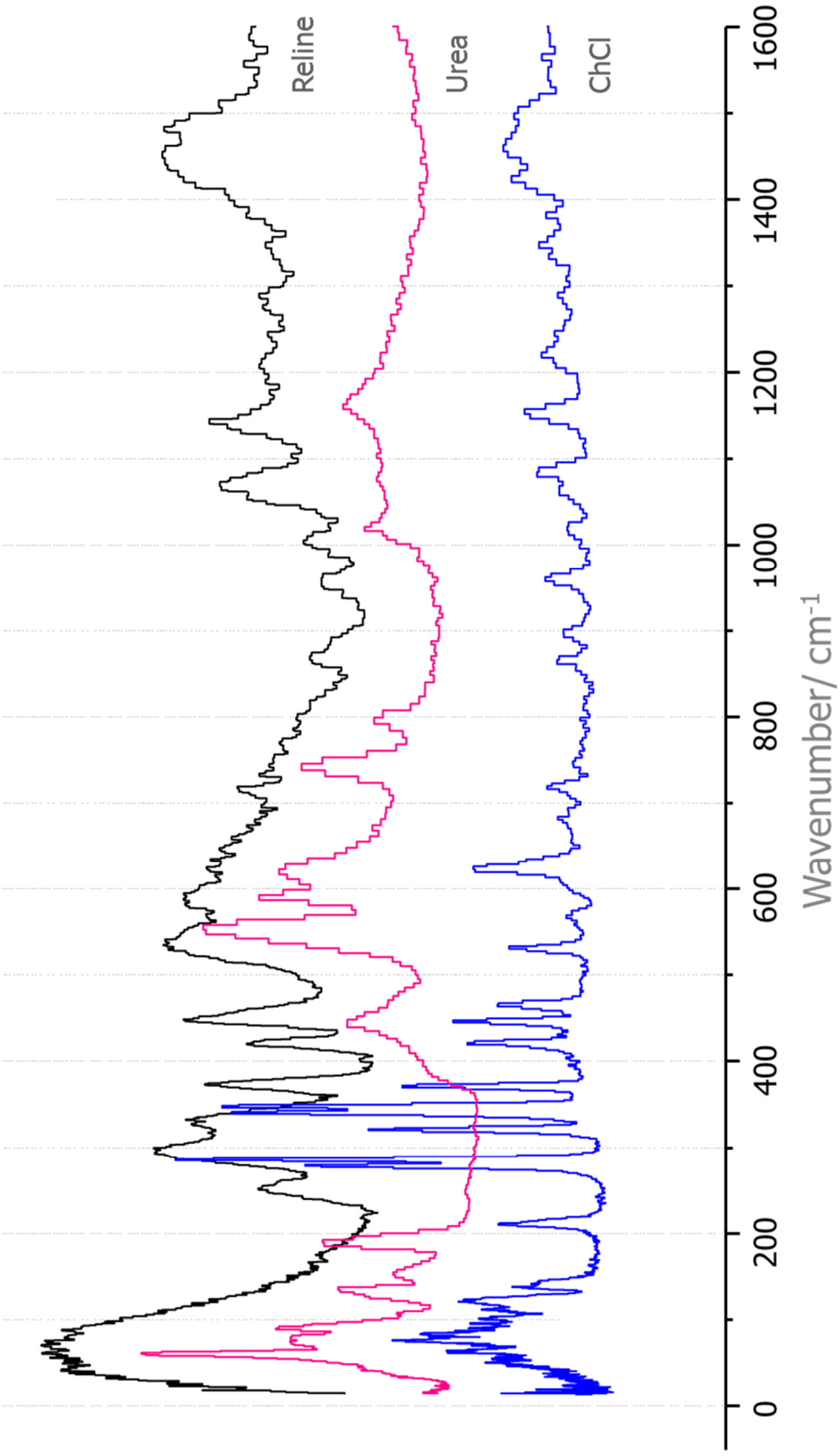

Figure S3. INS spectra of Reline, urea and choline chloride (ChCl), collected using MAPS with incident energy (Ei) of a) 806 cm-1, b) 2016 cm-1 and c) 5243 cm-1. Only small Q values in the range 0 ≤ Q ≤ 9 Å-1 are represented.

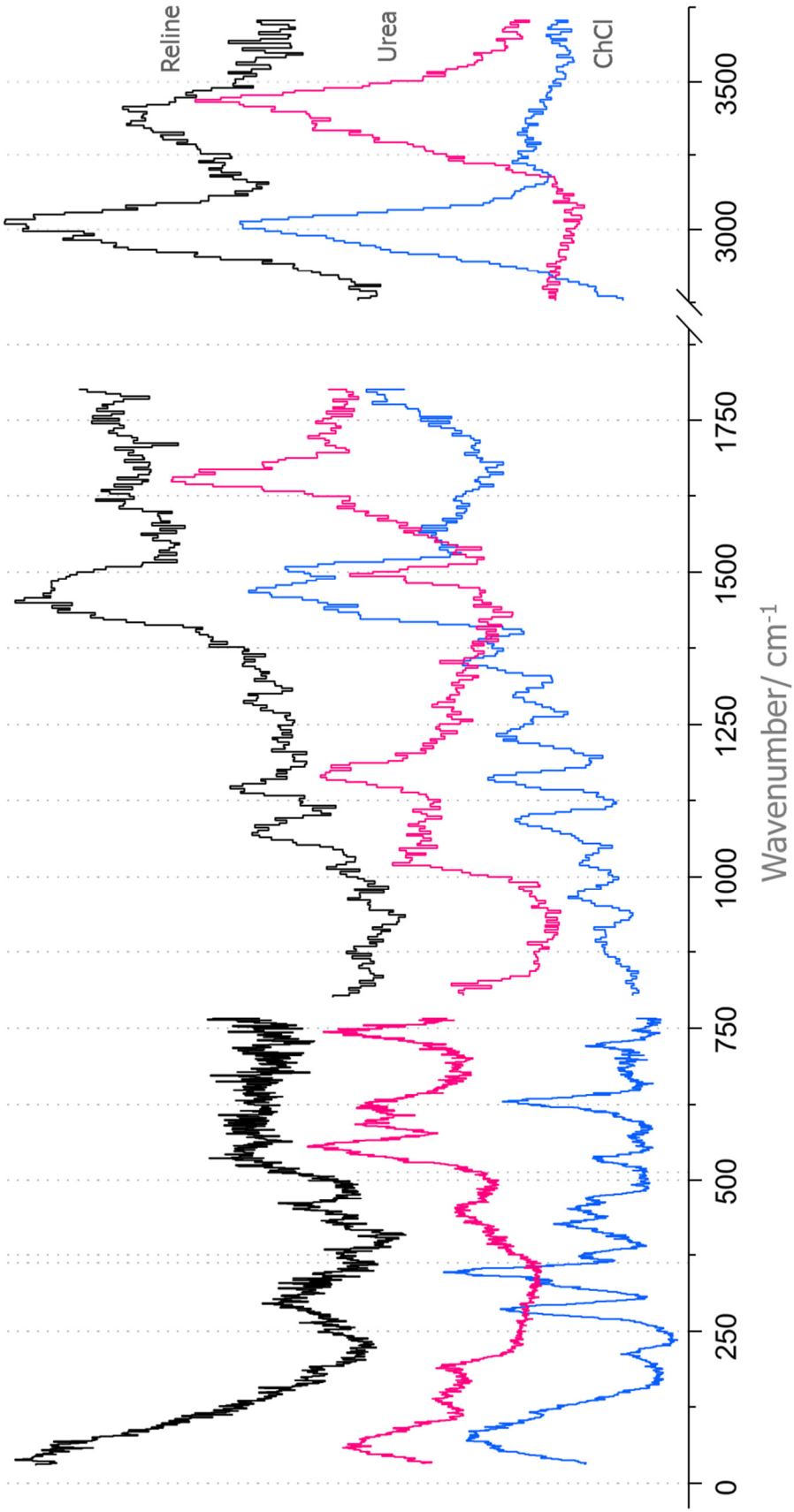

Figure S4. Dependence of energy resolution with energy transfer for the TOSCA instrument

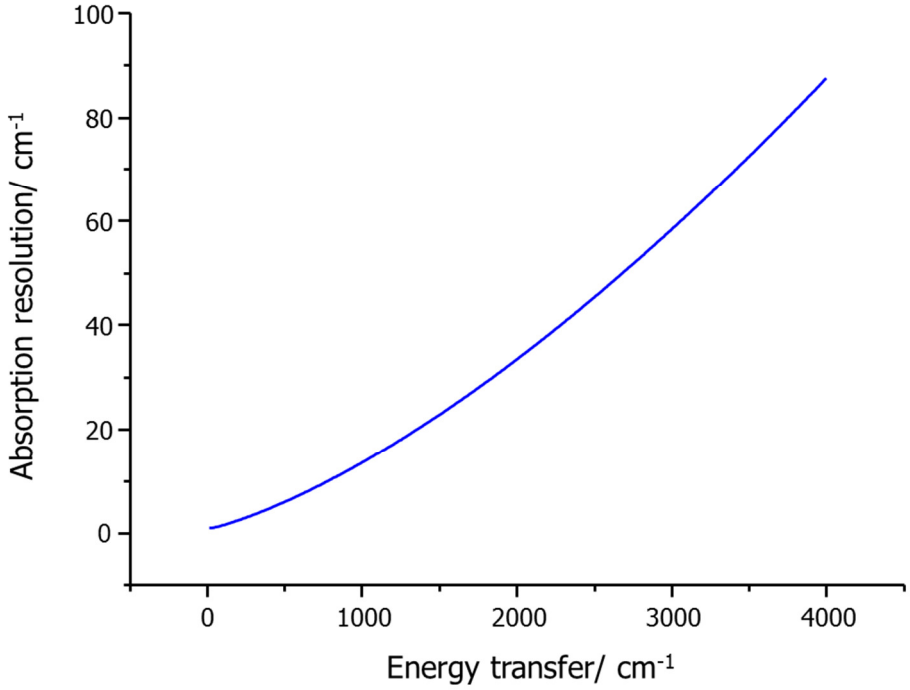

Figure S5. Raman spectra of urea (top), Reline (middle) and choline chloride (bottom)

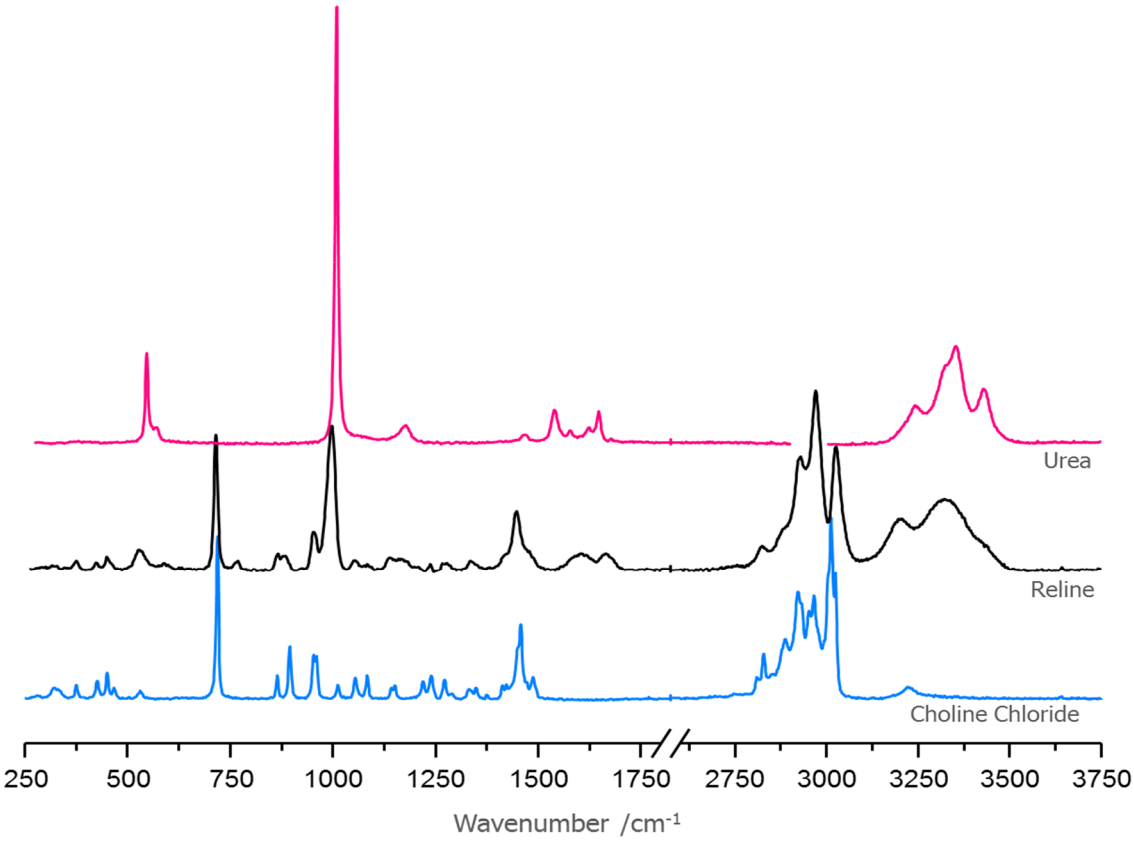

Figure S6. Comparison between Reline's experimental Raman spectrum and the one estimated by a discrete ab-initio calculation

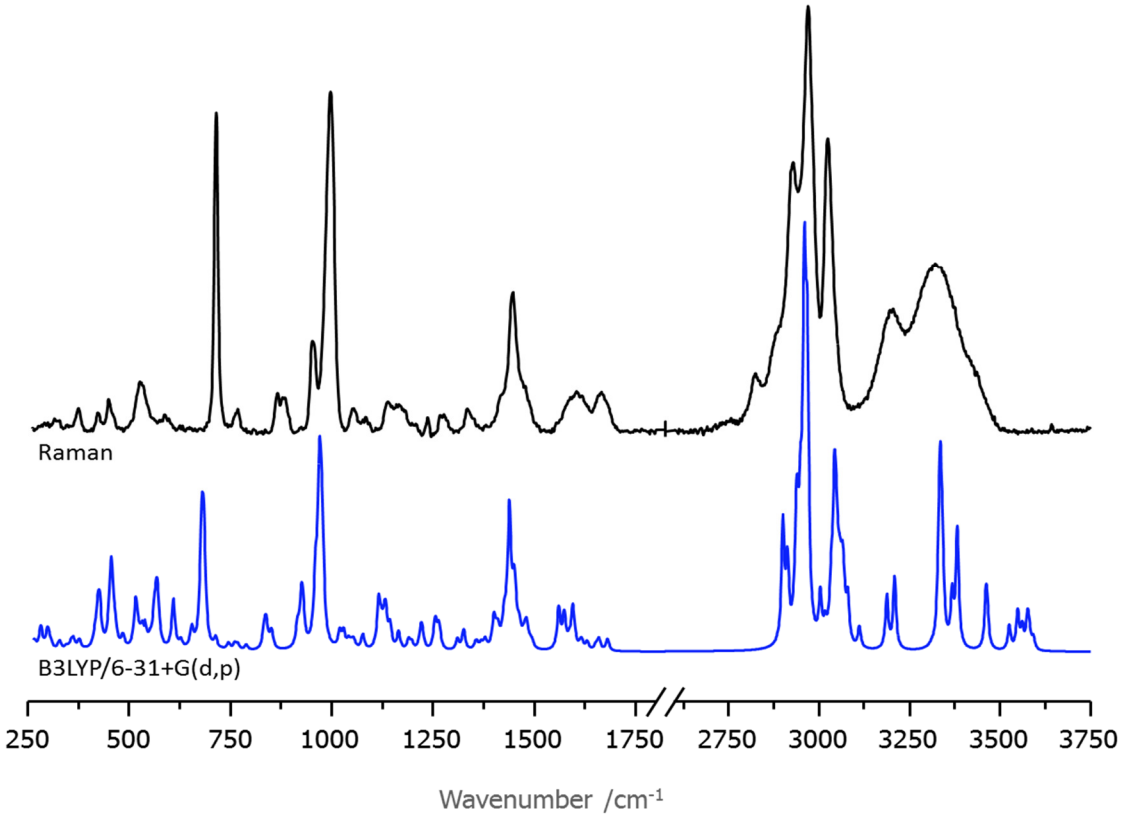

Figure S7. FTIR-ATR spectra of urea (top), Reline (middle) and choline chloride (bottom)

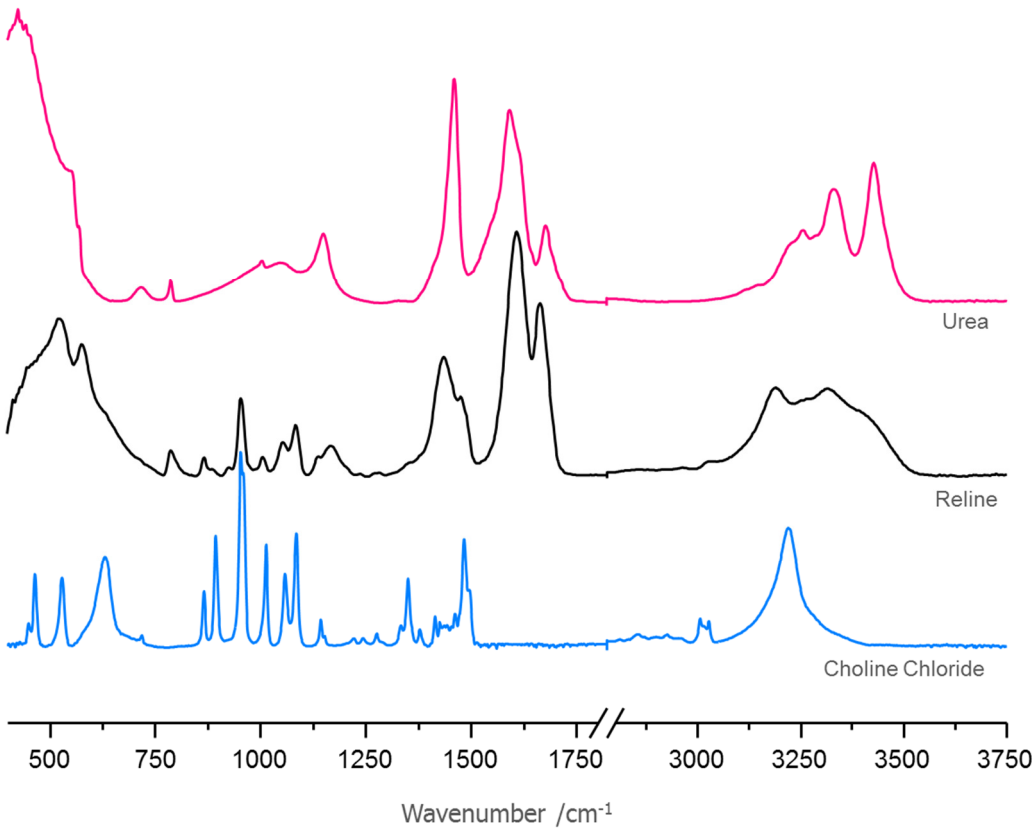

Figure S8. Comparison between Reline's experimental infrared spectrum and the one estimated by a discrete ab-initio calculation

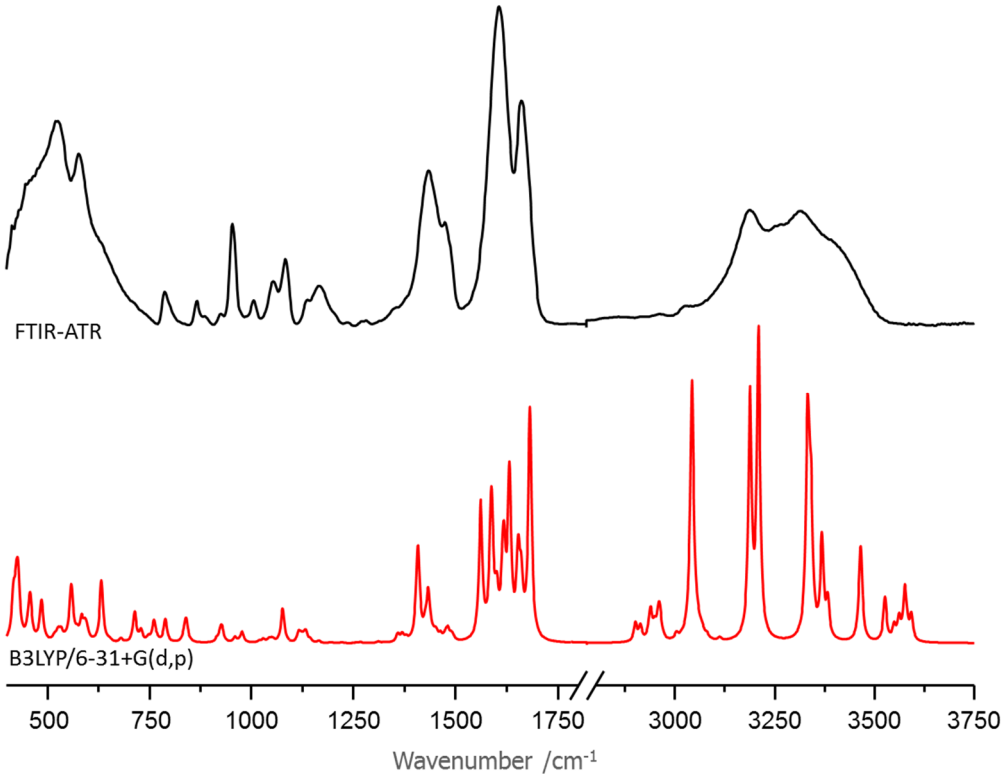

Figure S9. Raman spectra of Reline with increasing deuterium content

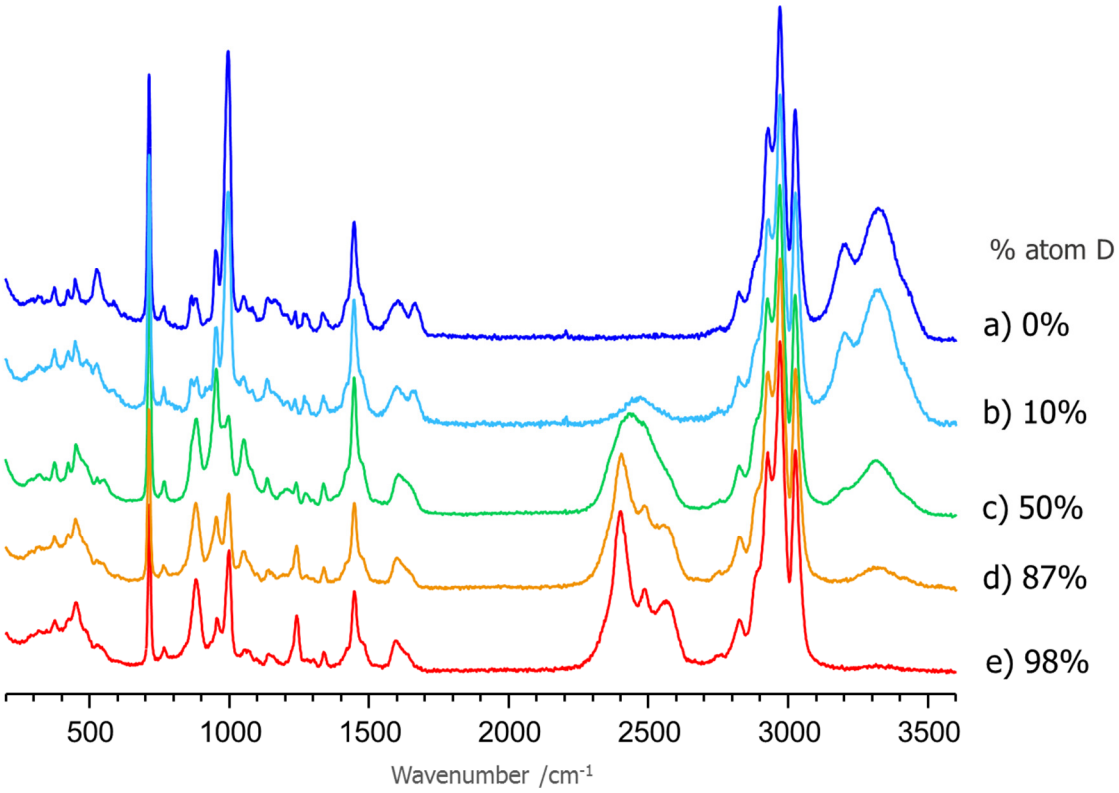

Figure S10. FTIR-ATR spectra of Reline with increasing deuterium content