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

"Infrared and Raman spectroscopy of non-conventional hydrogen bonding between N, N' disubstituted urea and thiourea groups: A combined experimental and theoretical investigation."

Supporting information

Table S1. Hydrogen bond lengths in **MUT** compared for single crystal diffraction (XRD) and first principles calculations (DFT) (values in Å)

MUT-XRD		**MUT-DFT simulation**	
IB	**DB**	**IB**	**DB**
SN2 3.34	**ON4 2.881**	**SN2 3.305**	**ON4 2.822**
SN1 3.52	**ON3 2.852**	**SN1 3.50**	**ON3 2.910**

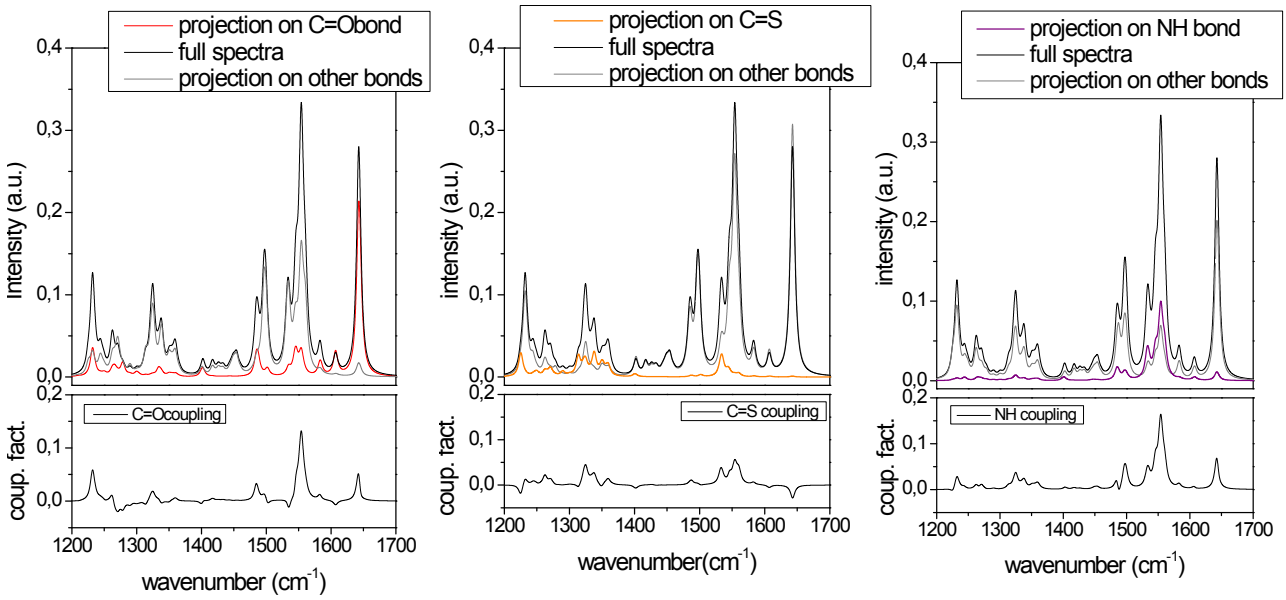

Figure S1. DFT infrared partial contribution to spectra for C=O, C=S and N-H bonds. Total spectra is given in black and the coupling coefficients of C=O, C=S and N-H bond vibration to vibrations involving other atomic groups are respectively given below.

Table S2.Raman vibration in the region of amides. . (Exp. =experimental, Calc. = calculation)

Exp.(cm^{-1}) 10K	Calc. (cm^{-1})	Principal assignment	Complement on assignment
589	578	thioamide V	asymmetric oop N-H bending involving ***DB*** (N3-H and N4-H) coupled to ν(C-N), ring vibration and a weak symmetric N-H bending involving ***IB***
579, 598	592 to 594	asymmetric ω(N-H)	involving ***DB*** (N3-H) and weak symmetric oop N-H bending involving ***IB*** (N1-H)
608	607	symmetric ω(N-H)	involving ***DB*** (N4-H and N3-H) and weak symmetric oop N-H bending involving ***IB*** (N2-H)
625	620	asymmetric ω(N-H)	involving ***DB*** (N4-H and N3-H) and weak symmetric oop NH bending involving ***IB*** (N1-H and N2-H)
644	644-656	amide V	symmetric oop N-H bending involving ***IB*** (N1-H and N2-H)
695	698-707	thioamide I	ν(C-S) ooupling with symmetric ω(N-H), involving ***IB*** and ***DB***
718	716	δ(C-H)	from aryl and butyl coupled to weak ν(C-S) and oop NH bending
	722-726	thioamide V	aymmetric oop N-H bending involving ***DB*** (N3-H and N4-H)
	730 740	thioamide V	aymmetric oop N-H bending in involving ***DB*** (N3-H and N4-H) and strong ω(NH) involving ***IB***
	763	Amide VI	ip δ(C=O) strongly attenuated by coupling
758	769	δ(C-H)	from butyl
1437	1432 to 1478	δ(C-H)	of $C-H_3$ and/or $C-H_2$ on butyl
1446 1462	1487	amide I	coupled with ν(C=C) vibration of aryl ring and ν(C-N)
1507	1499 to 1502	ν(C=C)	of aryl ring slightly coupled to ν(C=C) and to δ(N-H)
	1532	amide II	δ(N-H) involving ***DB*** (N3-H), coupling with ν(C=O) and weak δ(N-H) involving ***IB*** (N1-H and N2-H)
	1532b		
	1533	amide II	δ(N-H) involving ***DB*** (N3-H) and weakly involving IB (N1-H and N2-H)

	1534	ν(C=C)	in aryl ring coupled to δ(N-H) involving N1-H and N2-H
1557	1544	amide II and thioamide II	δ(N-H) involving ***DB*** (N3-H, N4-H) and ***IB*** (N2-H)
	1544’		
	1545		δ(N-H) involving ***DB*** (N3-H) and ***IB*** (N2-H)
1569	1547 to 1552		δ(N-H) involving ***DB*** (N3-H, N4-H) and ***IB*** (N2-H)
1591	1587 to1588		δ(N-H) involving ***DB*** (N3-H) and ***IB*** (N1-H) coupled to aryl
1610	1609 to 1609	ν(C=C)	in aryl ring slightly coupled to δ(N-H)
1658	1638	amide I	ν(C=O) coupled to ν(C=C) vibration of aryl ring
	1639		
1664	1647		
2869,2934, 2901,2964	2936 to 3021	ν(C-H)	involving C-H_2 in butyl group
	3050 to 3088		involving butyl C-H_3 in butyl group
3048,3082	3111 to 3158		involving C-H from Aryl
3160	3202 to 3212	asymmetric ν(N-H)	involving ***IB*** (N2-H) and ***DB*** (N3-H)
3287	3325 to 3327	asymmetric ν(N-H)	dominated by ***DB*** (N3-H)
	3364 to 3369		dominated by ***IB*** (N1-H)