Supplementary Information - The low energy phonon modes of the hydrogenated and deuterated π-conjugated system 7,7,8,8-tetracyanoquinodimethane: An inelastic neutron scattering study

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Table S1: The CASTEP calculated INS modes with their associated energies and corresponding irreproducible representations. The highlighted (blue) modes all have a calculated relative INS intensity above 0.5. The highlighted modes with energies between 0-40 meV have been given a numerical label and marked on Figures S1 and S2. Motion assignment was performed from examination of the CASTEP output for the modes up to 18 meV, incorporating all of the major lattice modes. Unassigned peaks are primarily intra-molecular in nature.

Energy (cm^{-1})	Energy (meV)	Irreducible representation	Relative intensity	Peak # TOSCA/ abINS >0.5 int.	Peak # PELICAN/ Aclimax >0.5 int.	Motion assignment	Experimental Data 298 K White *et al.* Ref. 23 in manuscript	Experimental Data 298 K Girlando and Pecile Ref. 22 in manuscript
-0.1	-0.01	Bu	-	-	-	Acoustic mode		
0.0	-0.01	Bu	-	-	-	Acoustic mode		
0.0	0.00	Au	-	-	-	Acoustic mode		
39.0	4.83	Bu	3.28	1	1	Translational lattice mode, minor contribution from butterfly motion		
43.6	5.40	Au	2.62	1	1	Translational lattice mode		
43.9	5.44	Ag	1.42	1	1	Librational lattice mode	40.5	76/41
65.3	8.09	Au	1.70	2	2	Translational lattice mode, minor contribution from butterfly motion		
66.1	8.20	Bg	1.23	2	2	Librational lattice mode	63	41/76
78.7	9.76	Ag	0.89	3	3	Librational lattice mode	74.5	97
80.7	10.00	Bg	1.15	3	3	Librational lattice mode, minor contribution from ring deformation	75.5	105
82.6	10.24	Au	0.68	3	3	Butterfly mode		
104.5	12.96	Ag	0.18	-	-	Torsion around C=C out of ring	96	144
105.9	13.13	Au	0.58	4	4	In-plane bending of C=C out of ring		
110.5	13.70	Bg	0.11	-	-	Torsion around C=C out of ring	104	133
111.8	13.86	Bu	0.44	-	-	Butterfly mode, minor contribution from molecular translation		
115.9	14.37	Bu	0.37	-	-	Out of ring C=C torsion/bend, minor contribution from molecular translation		
121.8	15.10	Au	0.79	5	5	Butterfly mode		
123.2	15.27	Bu	0.71	5	5	Butterfly mode		
134.9	16.73	Bg	0.42	-	-	Librational lattice mode, minor contribution from cyano-group scissoring		

144.6	17.93	Bu	0.35	-	-	Cyano-group scissoring, minor contribution from molecular translation		
145.4	18.03	Ag	0.99	6	6	C=C (out of ring) asymmetric bending		144
154.6	19.16	Bg	1.76	7	7			
158.4	19.64	Ag	0.37	-	-			
163.6	20.28	Bg	1.17	8	7			
164.5	20.40	Au	0.25	-	-			
165.4	20.51	Ag	2.74	8	7			
178.8	22.17	Bg	5.28	9	8			
179.4	22.24	Ag	4.68	9	8			
226.1	28.03	Bu	0.84	10	9			
230.8	28.61	Au	0.82	10	9			
288.6	35.78	Au	0.86	11	10			
292.3	36.24	Bu	0.83	11	10			
306.9	38.06	Ag	1.49	12	11			
307.3	38.10	Bg	1.53	12	11			
327.2	40.57	Bg	0.28					
329.5	40.85	Ag	0.28					
358.9	44.50	Ag	2.23					
360.0	44.63	Bg	2.16					
390.9	48.47	Bu	2.97					
391.4	48.52	Au	2.91					
431.5	53.50	Ag	0.32					
432.9	53.67	Bg	0.32					
454.0	56.28	Au	1.66					
455.1	56.42	Bu	1.62					
483.1	59.90	Au	3.46					
483.2	59.91	Bu	3.51					
500.7	62.08	Au	0.34					
503.0	62.36	Bu	0.35					
519.6	64.42	Ag	1.14					

521.4	64.65	Bg	1.14					
543.8	67.42	Bu	1.04					
544.9	67.56	Au	1.03					
599.6	74.34	Bg	0.37					
600.5	74.45	Ag	0.19					
601.7	74.61	Ag	0.41					
603.4	74.81	Bg	0.47					
603.9	74.88	Bu	0.17					
604.2	74.91	Ag	1.30					
604.2	74.91	Au	0.16					
605.0	75.01	Bg	1.05					
635.1	78.74	Au	1.44					
636.0	78.86	Bu	1.41					
718.4	89.07	Bg	0.95					
720.0	89.27	Ag	0.95					
758.5	94.04	Ag	0.94					
758.6	94.05	Bg	0.94					
830.6	102.98	Bg	6.39					
831.2	103.06	Ag	6.39					
870.6	107.94	Bu	4.49					
871.3	108.03	Au	4.50					
957.1	118.67	Ag	0.59					
958.7	118.86	Bg	0.59					
959.0	118.91	Bu	2.59					
959.4	118.95	Au	2.69					
988.8	122.60	Au	1.21					
988.9	122.61	Bu	1.31					
1013.6	125.67	Bu	4.47					
1014.1	125.74	Au	4.47					
1017.7	126.18	Bg	4.67					

1018.2	126.24	Ag	4.67					
1119.3	138.78	Bu	3.06					
1119.4	138.78	Au	3.10					
1182.6	146.63	Bg	0.64					
1182.9	146.66	Ag	0.64					
1194.8	148.14	Ag	5.95					
1195.3	148.20	Bg	5.94					
1198.5	148.59	Au	2.64					
1198.6	148.61	Bu	2.68					
1303.0	161.55	Ag	3.28					
1303.2	161.58	Bg	3.28					
1348.2	167.15	Bu	1.08					
1348.4	167.19	Au	1.08					
1385.3	171.76	Bu	2.53					
1386.0	171.84	Au	2.55					
1426.0	176.80	Ag	0.26					
1426.1	176.81	Bg	0.26					
1449.5	179.72	Bg	1.24					
1449.7	179.75	Ag	1.24					
1516.1	187.98	Bu	0.85					
1517.1	188.10	Au	0.81					
1522.9	188.81	Bu	0.53					
1523.3	188.87	Au	0.56					
1605.8	199.10	Ag	0.54					
1606.2	199.14	Bg	0.54					
2200.9	272.87	Bu	0.06					
2201.0	272.89	Bg	0.06					
2201.2	272.91	Au	0.06					
2201.3	272.93	Ag	0.06					
2219.9	275.24	Bu	0.06					

2220.5	275.31	Bg	0.06					
2221.7	275.45	Ag	0.06					
2223.6	275.69	Au	0.06					
3098.1	384.12	Bu	1.45					
3098.2	384.13	Au	1.45					
3099.5	384.29	Ag	1.44					
3099.9	384.33	Bg	1.45					
3107.3	385.26	Bu	1.41					
3107.4	385.27	Au	1.41					
3109.0	385.46	Ag	1.41					
3109.5	385.53	Bg	1.41					

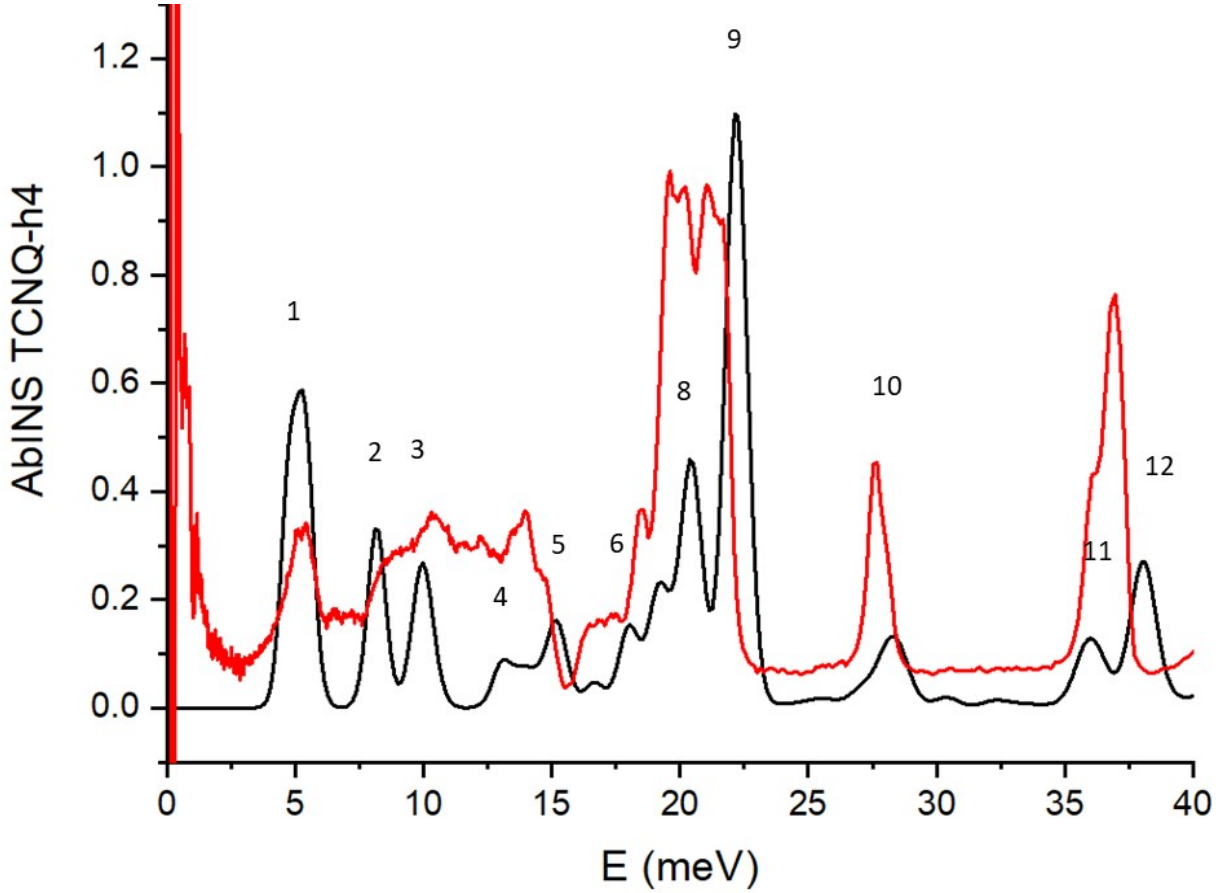

Figure S1: The hydrogenated TCNQ spectra (red) with the simulated spectra (black) in the low energy region where the peaks have been numbered that correspond to the vibration modes within Table S1. The small mismatch can be attributed to the calculation only incorporating the gamma point rather than the full Brillouin zone.

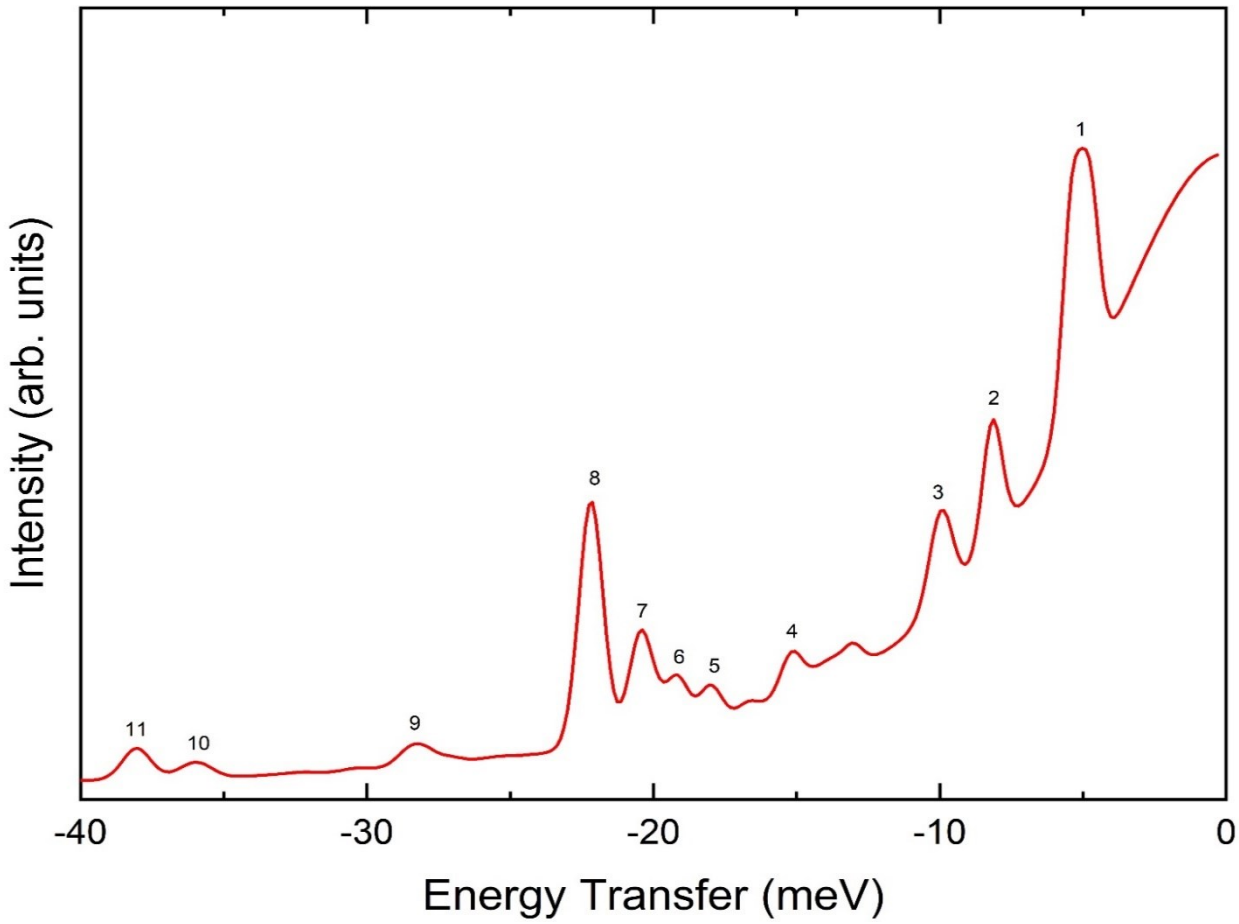

Figure S2: Calculated INS spectra for comparison with the 300 K data set with the peaks labelled to correspond to the calculated modes labelled in Table S1.

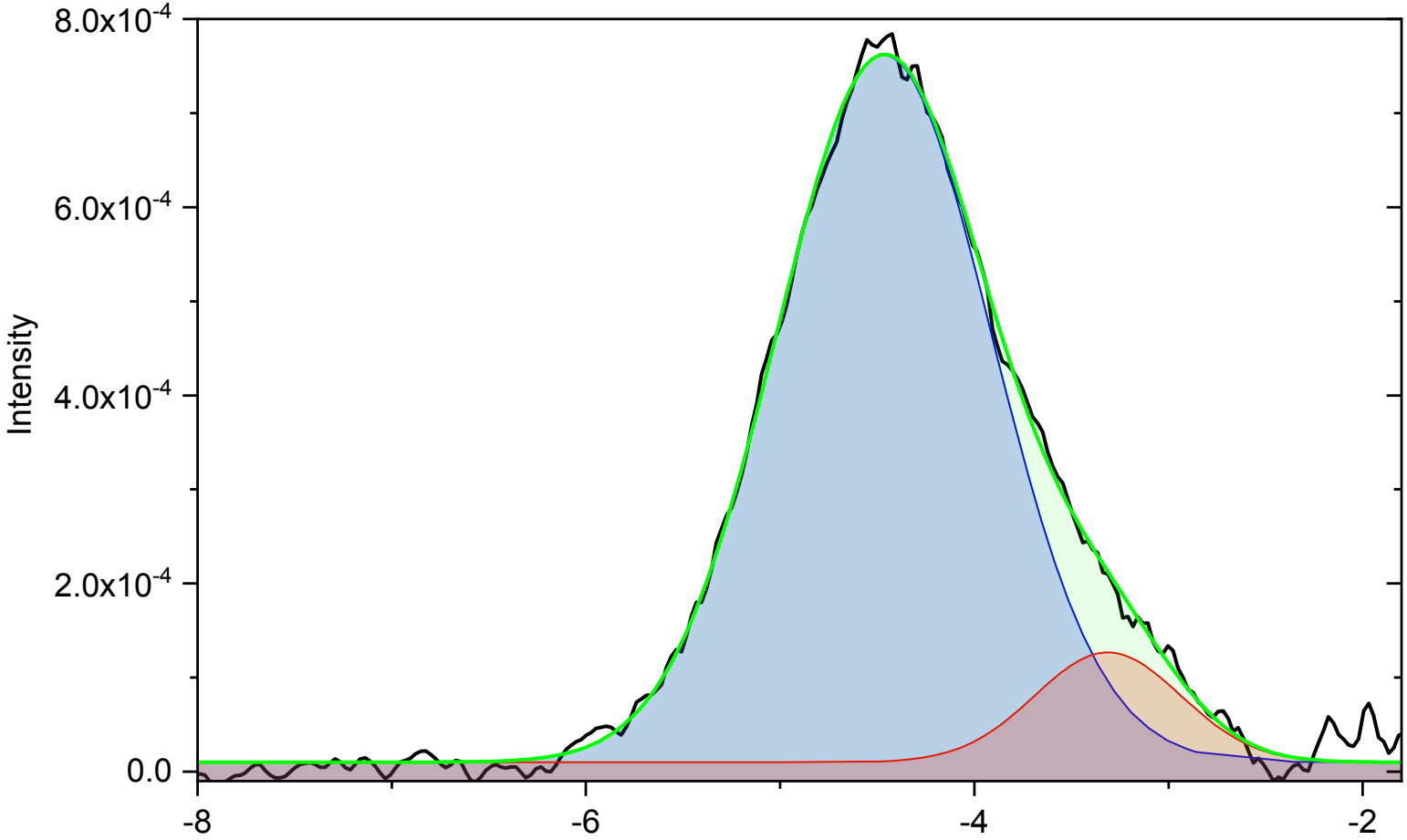

Figure S3: Fit to the 300 K TCNQ-H_4 INS spectra collected on PELICAN. Note that the background has been subtracted.