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Supporting information for article:

X-ray diffraction data as a source of the vibrational free energy contribution in polymorphic systems.

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	Y_5K	Y_100	Y_125K	Y_150K	Y_175K	Y_200K	Y_295K
Chemical formula	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$
M_r	295.06	295.1	295.1	295.1	295.1	295.1	295.1
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
Temperature (K)	5	100	125	150	175	200	295
***a*, *b*, *c* (Å)**	9.510 (1), 4.2473 (4), 7.7107 (8)	9.5239 (3), 4.2565 (1), 7.7584 (2)	9.5185 (4), 4.25574 (15), 7.7749 (3)	9.5271 (2), 4.26073 (9), 7.7960 (2)	9.5357 (3), 4.26613 (13), 7.8240 (3)	9.5488 (2), 4.27352 (11), 7.8524 (3)	9.5911 (3), 4.29992 (13), 7.9669 (3)
α, β, γ (°)	112.420 (5), 95.8100 (5), 106.1630 (5)	112.869 (2), 95.579 (2), 106.205 (2)	112.961 (4), 95.635 (3), 106.167 (3)	113.185 (2), 95.505 (2), 106.1658 (19)	113.317 (3), 95.508 (3), 106.125 (3)	113.547 (3), 95.379 (2), 106.125 (2)	114.358 (3), 94.954 (3), 106.143 (3)
***V* (Å^3)**	268.88 (5)	270.65 (1)	270.80 (2)	271.72 (1)	273.03 (2)	274.47 (1)	279.82 (2)
Z	1	1	1	1	1	1	1
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.62	0.62	0.62	0.62	0.61	0.61	0.61
Crystal size (mm)	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05	0.1 × 0.05 × 0.05
Diffractometer	Bruker *APEX*-II CCD	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos
Absorption correction	Multi-scan *SADABS2014*/4	Multi-scan *CrysAlis PRO*,SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*,SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*,SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*,SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*,SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*,SCALE3 ABSPACK
T_{min}, T_{max}	0.644, 0.748	0.726, 1.000	0.906, 1.000	0.882, 1.000	0.844, 1.000	0.833, 1.000	0.746, 1.000
No. of measured, independent and observed [> 2.0σ(*I*)] reflections	8746, 2614, 2389	17402, 1810, 1695	21217, 2752, 2609	21308, 2757, 2589	21405, 2756, 2545	21542, 2767, 2535	21554, 3041, 2510
R_{int}	0.039	0.037	0.023	0.024	0.025	0.026	0.028
(sin θ/λ)$_{max}$(Å^{-1})	0.867	0.752	0.853	0.853	0.857	0.858	0.880
R*[F^2 > 2σ(F^2)], *wR*(F^2), *S	0.037, 0.169, 3.55	0.019, 0.048, 1.28	0.017, 0.047, 1.33	0.019, 0.052, 1.43	0.022, 0.057, 1.50	0.025, 0.063, 1.60	0.050, 0.115, 2.32
No. of reflections	2613	1810	2752	2757	2756	2767	3041
No. of parameters	98	98	98	98	98	98	98
No. of restraints	11	11	11	11	11	11	11
(Δ/σ)$_{max}$	0.083	−0.050	−0.043	−0.050	−0.055	−0.050	−0.141
Δρ$_{max}$, Δρ$_{min}$(e Å^{-3})	0.74, -1.20	0.27, −0.35	0.38, −0.29	0.44, −0.35	0.46, −0.41	0.53, −0.47	0.73, −0.55

	W_5	**W_100**	**W_125**	**W_150**	**W_175**	**W_200**	**W_RT**
Chemical formula	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$	$C_{10}H_8Cl_2O_6$
M_r	295.08	295.08	295.08	295.08	295.08	295.08	295.08
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
Temperature (K)	5	100	125	150	175	200	294
***a*, *b*, *c* (Å)**	9.8021 (4), 7.7322 (4), 10.4934 (5)	9.8043 (4), 7.7484 (4), 10.5027 (5)	9.8090 (4), 7.7577 (3), 10.5083 (5)	9.8127 (2), 7.76700 (16), 10.5170 (3)	9.8178 (2), 7.77841 (17), 10.5270 (3)	9.8231 (2), 7.79072 (17), 10.5376 (3)	9.8461 (3), 7.84791 (19), 10.5783 (3)
α, β, γ (°)	116.848 (4), 124.3970 (4), 88.7890 (3)	116.731 (4), 124.349 (4), 88.853 (3)	116.688 (5), 124.329 (5), 88.869 (4)	116.638 (2), 124.323 (3), 88.869 (2)	116.595 (2), 124.299 (3), 88.884 (2)	116.557 (2), 124.277 (3), 88.896 (2)	116.412 (3), 124.159 (3), 88.976 (2)
***V* (Å^3)**	555.15 (1)	557.98 (1)	559.65 (4)	561.46 (2)	563.58 (2)	565.79 (2)	575.36 (3)
Z	2	2	2.0	2.0	2.0	2.0	2
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.60	0.60	0.60	0.60	0.59	0.59	0.58
Crystal size (mm)	2.0 × 0.5 × 0.35	2.0 × 0.5 × 0.35	2.0 × 0.5 × 0.35	2.0 × 0.5 × 0.35	2.0 × 0.5 × 0.35	2.0 × 0.5 × 0.35	2.0 × 0.5 × 0.35
Diffractometer	Bruker *SMARTAPEX2* a rea detector	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos	SuperNova, Single source at offset, Eos
Absorption correction	Multi-scan *SADABS2014*/4	Multi-scan *CrysAlis PRO*, SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*, SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*, SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*, SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*, SCALE3 ABSPACK	Multi-scan *CrysAlis PRO*, SCALE3 ABSPACK
T_{min}, T_{max}	0.647, 0.748	0.473, 1.000	0.549, 1.000	0.534, 1.000	0.586, 1.000	0.586, 1.000	0.574, 1.000
No. of measured, independent and observed [> 2.0σ(*I*)] reflections	24786, 7048, 6026	96497, 5428, 4931	20138, 2810, 2564	65857, 5858, 5141	66140, 5867, 5015	66436, 5848, 4866	62436, 6432, 4511
R_{int}	0.039	0.050	0.039	0.041	0.042	0.042	0.049
(sin θ/λ)$_{max}$(Å^{-1})	0.927	0.856	0.691	0.880	0.882	0.880	0.880
R*[*F*^{2} > 2σ(*F*^{2})], *wR*(*F*^{2}), *S	0.027, 0.077, 1.47	0.023, 0.055, 1.30	0.023, 0.051, 1.18	0.025, 0.057, 1.26	0.027, 0.059, 1.26	0.028, 0.062, 1.29	0.037, 0.080, 1.35
No. of reflections	7048	5428	2810	5858	5867	5848	6432
No. of parameters	195	195	195	195	195	195	195
No. of restraints	16	16	16	16	16	16	16
Δρ$_{max}$, Δρ$_{min}$(e Å^{-3})	0.68, −0.93	0.45, −0.37	0.26, −0.38	0.34, −0.49	0.36, −0.42	0.36, −0.41	0.42, −0.48

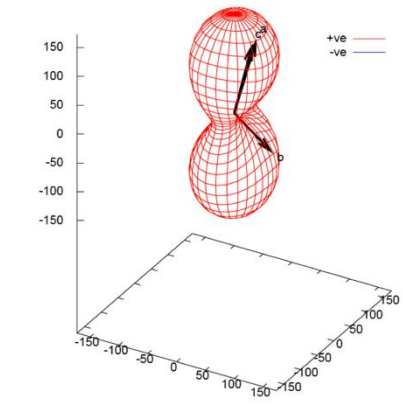
White form

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-14.0733	1.0337	0.0128	0.9381	0.3461
X_2	51.4334	3.3494	0.7531	0.6490	0.1077
X_3	172.6677	7.7985	0.1192	-0.4907	0.8631
V	214.9940	12.0275			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

Rotate +x | Rotate -x | Rotate +z | Rotate -z | Down X_1 | Down X_2 | Down X_3 | Value X:30 | Value Z:60



Yellow form

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	22.0416	0.1326	-0.9609	-0.2094	0.1811
X_2	43.3472	0.9798	0.6159	-0.4444	0.6505
X_3	94.5403	0.5836	0.3214	0.7465	0.5827
V	162.0085	1.8874			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

Rotate +x | Rotate -x | Rotate +z | Rotate -z | Down X_1 | Down X_2 | Down X_3 | Value X:30 | Value Z:60

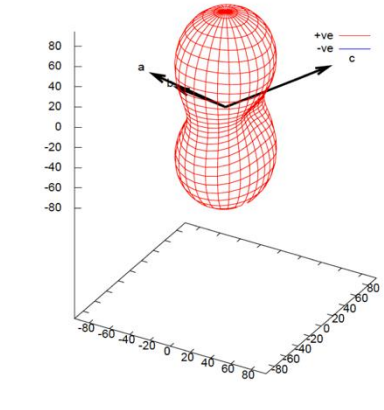


Figure S1. Expansivity indicatrices calculated by the PASCal software. (Cliffe & Goodwin, 2012) Left: White form. Right: Yellow form.

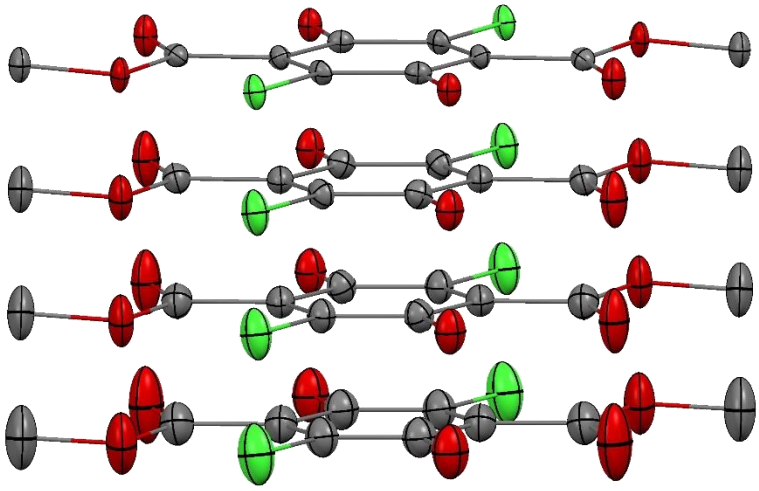
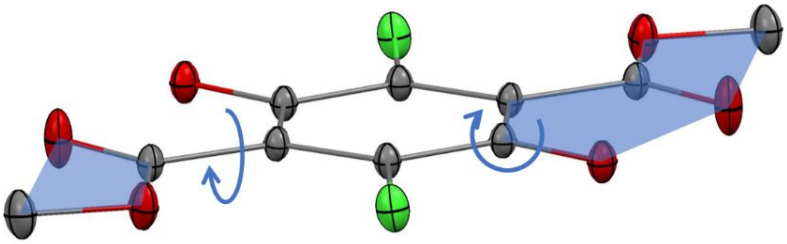
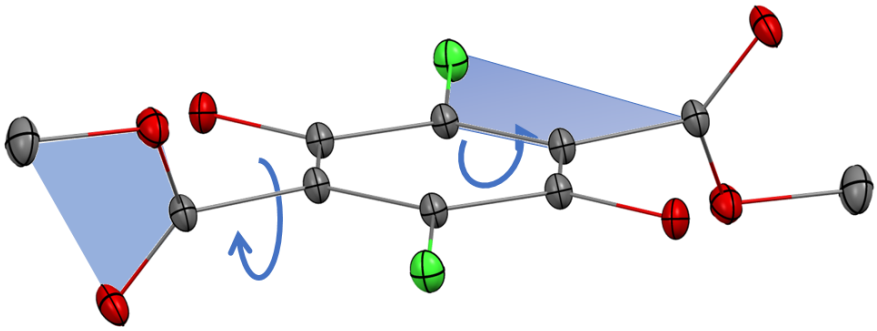


Figure S2. ADPs obtained by Dunitz and co-workers for Y polymorph



(a)



(b)

Figure S3. Description of internal vibrational modes in NKA models for yellow (a) and white (b).

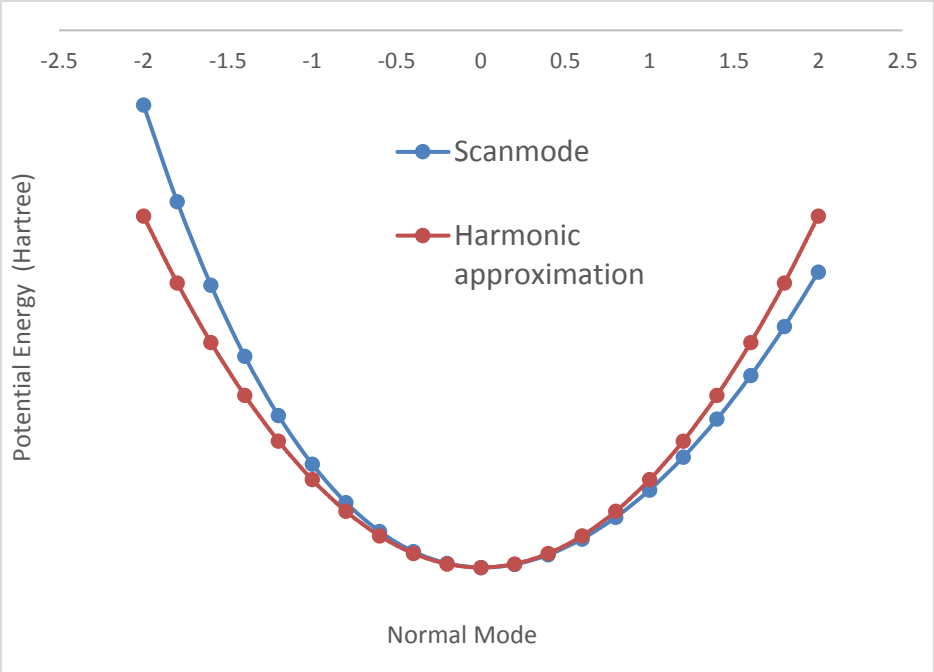
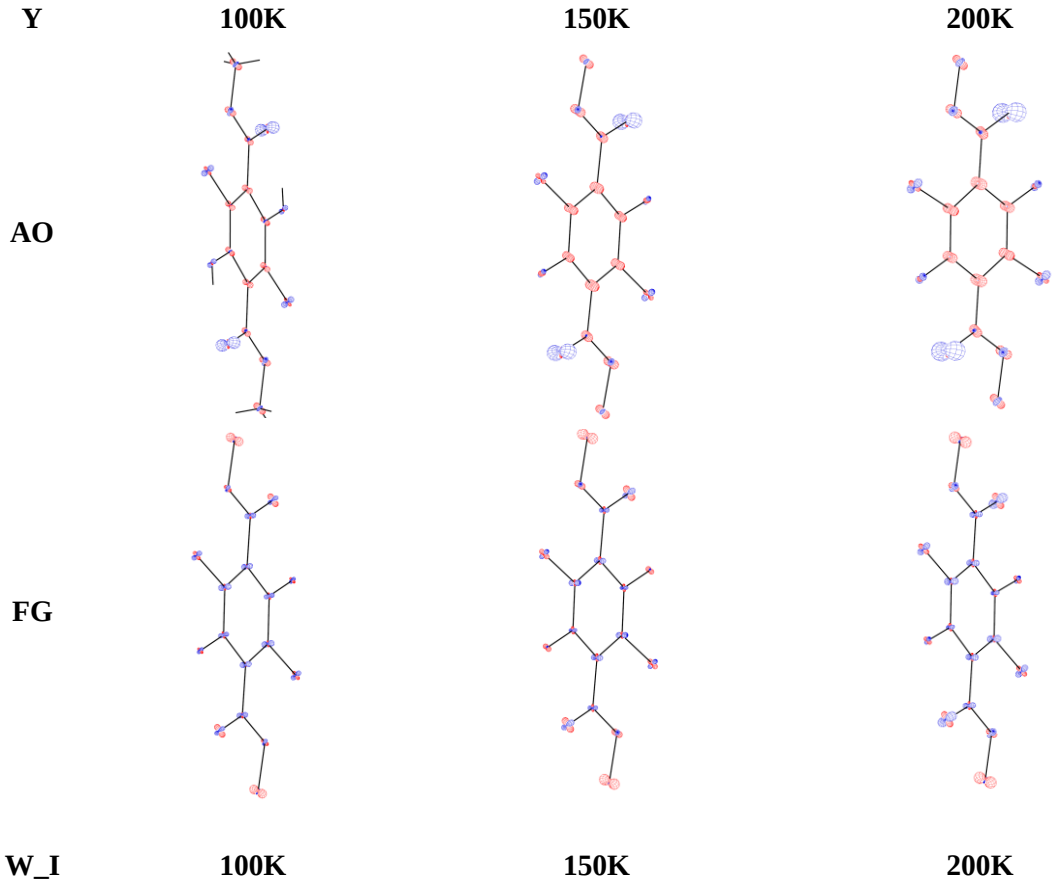
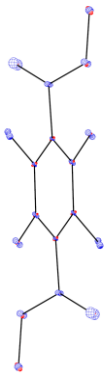


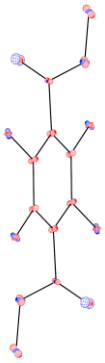
Figure S4. Energy scan along normal mode vector for Y, mode number 5.

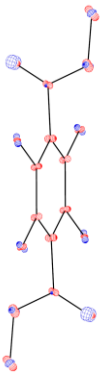
Figure S5. PEANUT plots – difference between models from *NoMoRe* and from routine X-ray refinements (*Scaling applied in PEANUT 3.08*).



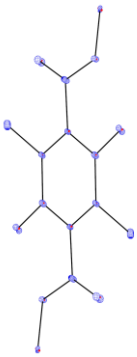
AO

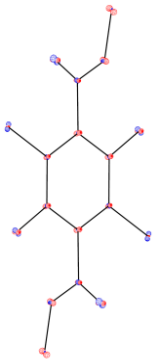


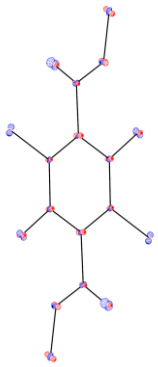




FG

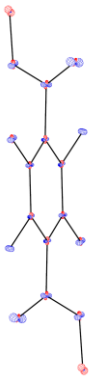


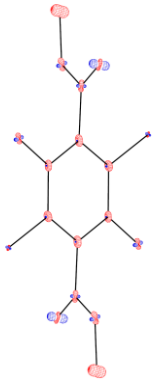


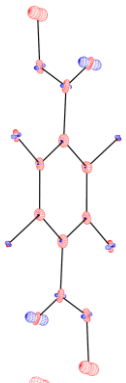


W_II **100K** **150K** **200K**

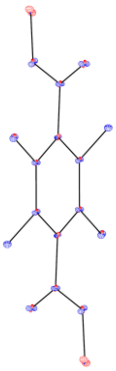
AO

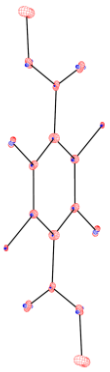






FG





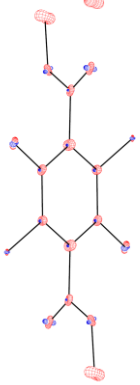


Table S2. Final statistics and frequencies obtained for yellow and white after NKA refinement

Polymorph	Model	Statistics after refinement: Observations/Restrains/Parametrs R2ij	Frequencies (cm^{-1})	Gruneisen parameters	Main Eigenvector components
Yellow	TLS+	756 / 39 /82	35 (1)	7.0(3)	54% Lx + 46% Ly
	gruneisen+	R2ij: 0.084	48 (1)		95% Lz
	internal_modes (see Fig		76 (7)		45% Lx + 50% Ly + 5% Lz
	S2a)		47 (2)	5.0(8)	Tx
			49 (2)	6.2(8)	Ty
			37 (1)	5.0(2)	**50% Tz + 50% U1**
White	TLS+	756 / 39 / 80	36(1)		27% Lx + 73% Ly
	gruneisen+	R2ij: 0.078	53(2)	7.1(6)	5% Lx + 92% Lz
Molecule 1	internal_modes (see Fig		79(7)		68% Lx + 25% Ly + 8% Lz
	S2b)		35(1)		85% Tx + 13% Ty
			33(1)		14% Tx + 84% Ty
			48(2)	4.7(8)	**63% Tz + 16% U1 + 20% U2**
White	TLS+	756 /39 / 81	65(2)		35% Lx + 32% Ly + 32% Lz
	gruneisen+	R2ij: 0.076	58(2)	5.1(8)	37% Lx + 61% Lz
Molecule 2	internal_modes (see Fig		35(1)		28% Lx + 65% Ly
	S2b)		36(1)		83% Tx + 5% Ty + 9% Tz **+ 3% U1**
			32(1)		6% Tx + 93% Ty
			51(2)	5.7(6)	**9% Tx + 71% Tz + 14% U2 + 3% U1**

U1 = Butterfly motion; U2 = COO group rotation

Table S3. Energies computed for Y and W from supercell and Γ point DFT computations.

300K	E_Y **Supercell**	E_Y **Γ**	E_W **supercell**	E_W **Γ**
E_{total} /kJ·mol^{-1}	-4611791	-4611779	-9223583	-9223566
$E_{electronic}$/kJ·mol^{-1}	-4612228	-4612213	-9224447	-9224419
ST/kJ·mol^{-1}	85,8	77,5	177,6	176,9
ZPE/kJ·mol^{-1}	476,5	470,3	947,5	938,2
H_{vib}/kJ·mol^{-1}	45,3	41,4	93,5	91,9

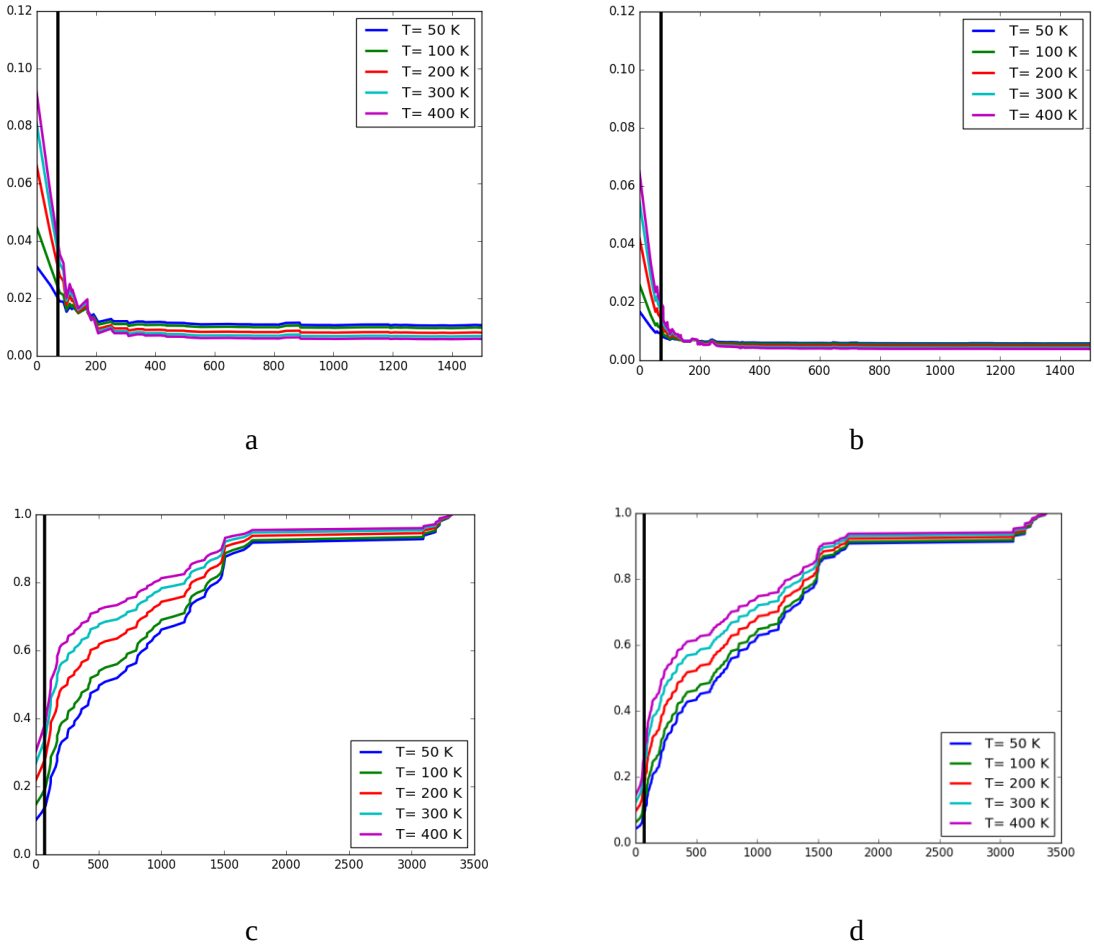


Figure S6. Contribution of given frequency to Uiso for **Y** and **W (a)** and **(b),** cumulative contribution of frequencies to Uiso for **Y** and **W (c)** and **(d).**

References

Cliffe, M. J. & Goodwin, A. L. (2012). *J. Appl. Crystallogr.* **45**, 1321–1329.