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Supporting information for article:

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Supporting Information

Influence of the refinement strategies on the wave functions derived from experiment

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Table S1. ADPs for SO_2 with different sigma cutoffs applied.

n	Uxx	Uyy	Uzz	Uxy	Uxz	Uyz
Sulphur						
0	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
1	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
2	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
3	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
4	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
Oxygen						
0	0.02399(10)	0.02650(10)	0.03300(11)	0.00475(10)	0.00323(16)	-0.00679(13)
1	0.02399(11)	0.02650(11)	0.03300(11)	0.00475(10)	0.00323(17)	-0.00679(14)
2	0.02399(11)	0.02650(11)	0.03300(11)	0.00475(10)	0.00322(17)	-0.00679(14)
3	0.02399(11)	0.02650(12)	0.03300(12)	0.00475(11)	0.00322(18)	-0.00678(14)
4	0.02400(11)	0.02650(12)	0.03300(12)	0.00475(11)	0.00321(18)	-0.00678(14)

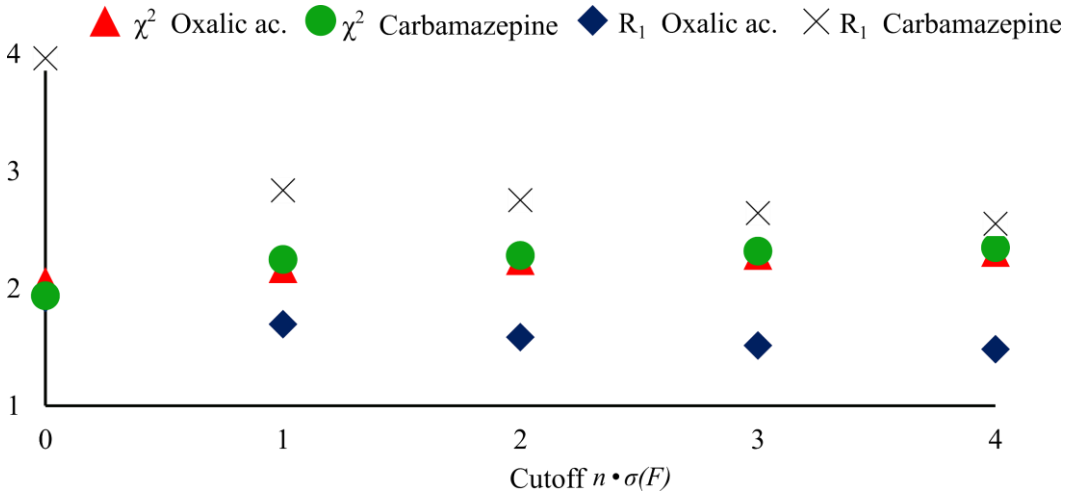


Figure S1. The χ^2 and R1(%) values for different $F < n \cdot \sigma(F)$ (with n= 0−4) cutoffs applied to oxalic acid and carbamazepine.

Table S2. Percentage of reflections used for each $F < n \cdot \sigma(F)$ (with n= 0−4) cutoff.

n	SO_2	Urea	Carbamazepine	Oxalic acid
0	1080 (100.0%)	1045 (100.0%)	16011 (100.0%)	3051 (100.0%)
1	957 (88.6%)	817 (78.2%)	13546 (84.6%)	2878 (94.3%)

2	909 (85.2%)	817 (78.2%)	13287 (83%)	2769 (90.8%)
3	855 (79.2%)	817 (78.2%)	12959 (80.1%)	2694 (88.3%)
4	825 (76.4%)	817 (78.2%)	12638 (79.8%)	2652 (86.9%)

Table S3. ADPs for SO_2 with different resolution cutoffs applied.

Resolution ($Å^{-1}$)	Uxx	Uyy	Uzz	Uxy	Uxz	Uyz
Sulphur						
0.60	0.0192(3)	0.0159(2)	0.01716(11)	0.00167(8)	0.00000	0.00000
0.71	0.01918(14)	0.01595(12)	0.01747(15)	0.00163(11)	0.00000	0.00000
1.00	0.01934(5)	0.01631(5)	0.01725(4)	0.00179(5)	0.00000	0.00000
Full	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
Oxygen						
0.60	0.0242(3)	0.0266(4)	0.0332(3)	0.0048(3)	0.0017(7)	-0.0070(5)
0.71	0.0241(2)	0.0264(3)	0.0331(2)	0.0049(2)	0.0029(4)	-0.0069(3)
1.00	0.02393(14)	0.02644(14)	0.03293(14)	0.00475(13)	0.0032(2)	-0.00677(19)
Full	0.02399(10)	0.02650(10)	0.03300(11)	0.00475(10)	0.00323(16)	-0.00679(13)

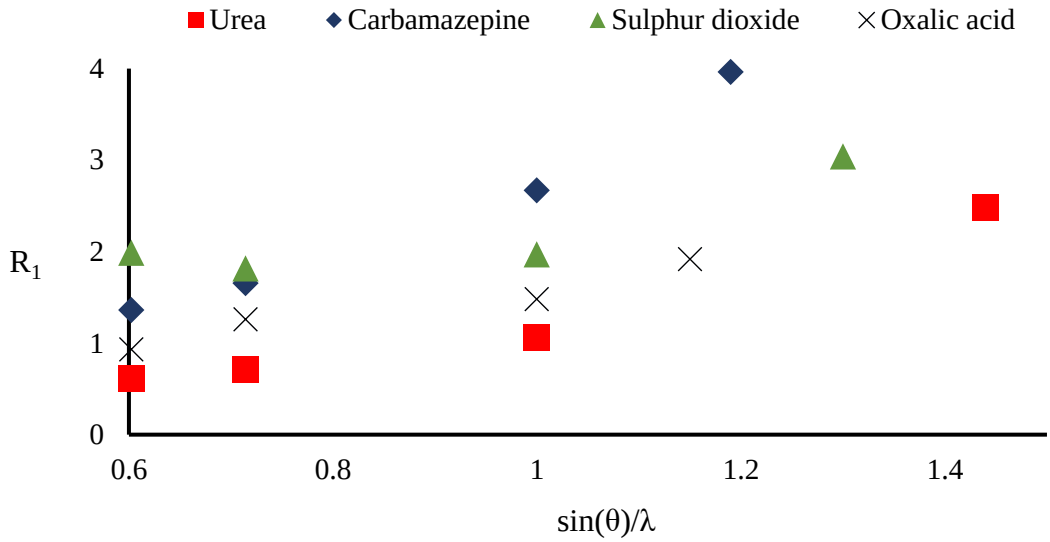


Figure S2. The R_1 (%) for urea, carbamazepine, sulphur dioxide and oxalic acid for different resolution cutoffs. The last values correspond to the full data set, which is different for each system.

Table S4. Percentage of reflections kept for each resolution cutoff

n	SO_2	Urea	Carbamazepine	Oxalic acid
Full	1080 (100.0%)	1045 (100.0%)	16011 (100.0%)	3051 (100.0%)
1.00	496 (45.9%)	402 (38.5%	9555 (59.7%)	2028 (66.5%)
0.71	188 (17.4%)	159 (15.2%)	3485 (21.8%)	734 (24.1%)

0.60	115 (14.4%)	102 (9.8%)	2088 (13.0%)	446 (14.6%)

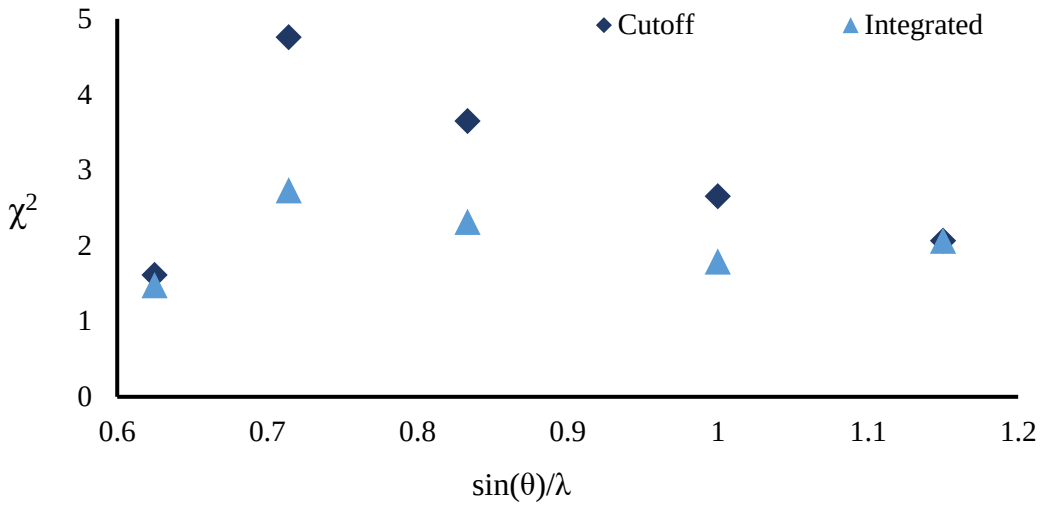


Figure S3. The χ^2 for oxalic acid with the application of resolution cutoffs and reintegration of data up to the corresponding resolution.

Computation of σ(F) from σ(F^2): The following procedure is implemented in *Tonto* for transforming σ(F) when the input data is in introduced in F^2

If $F^2 > \sigma(F^2)$ then

$S^+ = -F + (F^2 + \sigma(F^2))^{1/2}$

$S^- = F - (F^2 - \sigma(F^2))^{1/2}$

else

$S^+ = -F + (F^2 + \sigma(F^2))^{1/2}$

$S^- = F$

end

$\sigma(F) = MAX(S^+, S^-)$

In SHELX, the transformation is performed by the equation:

$$\sigma(F) = \sqrt{2}\,\frac{\sigma(F^2)}{2\,F}$$

This expression can be problematic for very low *F* values, for which further corrections are necessary (Sheldrick, G. M., & Schneider, T. R. (1997). Methods Enzymol., 277, 319-343. Watkin, D. (2008). J. Appl. Cryst., 41, 491–522).

Table S5. Comparison of the geometric parameters and residual factors of HAR of the full data of SO^2, for refinements **I-IV**.

Refinement	Uxx	Uyy	Uzz	Uxy	Uxz	Uyz
Sulphur						
I disp. included in the model	0.01974(3)	0.01683(3)	0.01769(3)	0.00182(3)	0	0
II disp. not included in the model	0.01941(3)	0.01652(3)	0.01736(3)	0.00182(4)	0	0
III disp. not included in the model	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0	0
IV disp. not included in the model	0.01942(4)	0.01652(3)	0.01737(3)	0.00181(4)	0	0
Oxygen						
I disp. included in the model	0.02378(9)	0.02626(9)	0.03283(11)	0.00453(8)	0.00344(12)	-0.00656(12)
II disp. not included in the model	0.02401(10)	0.02650(10)	0.03302(11)	0.00474(10)	0.00321(16)	-0.00675(13)
III disp. not included in the model	0.02399(10)	0.02650(10)	0.03300(11)	0.00475(10)	0.00323(16)	-0.00679(13)
IV disp. not included in the model	0.02394(10)	0.02646(11)	0.03303(13)	0.00463(10)	0.00347(14)	-0.00665(14)

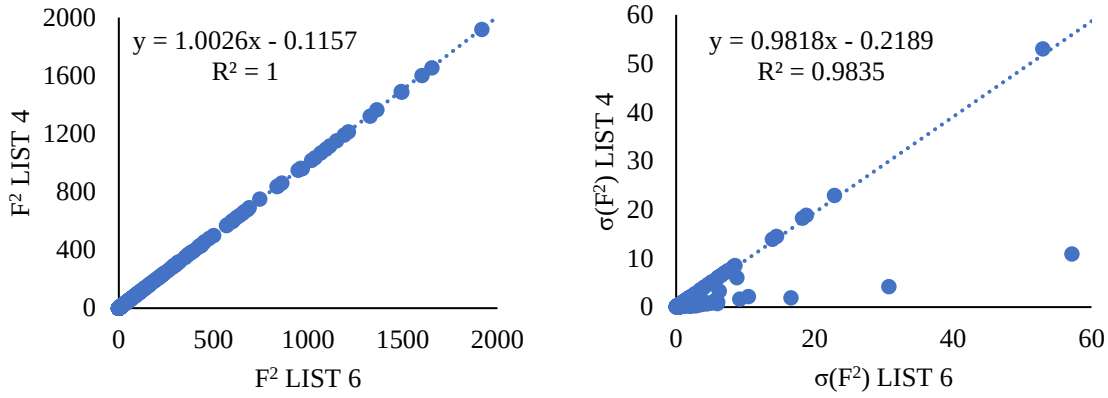
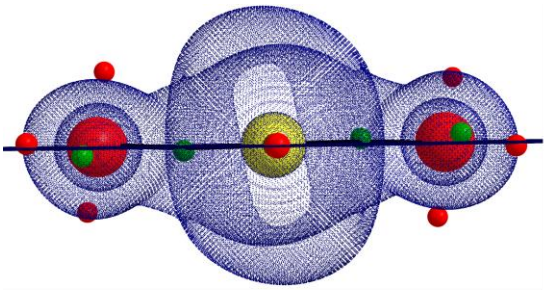


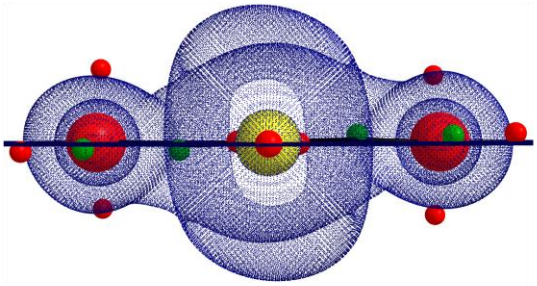
Figure S4. Comparison of the F^2 (top) and $\sigma(F^2)$ (bottom) obtained from the SHELX by merging reflections with (LIST 6) and without (LIST 4) dispersion correction.

Table S6. ADPs for SO_2 using Tonto, and Olex2 with two different weighting schemes (w. s.).

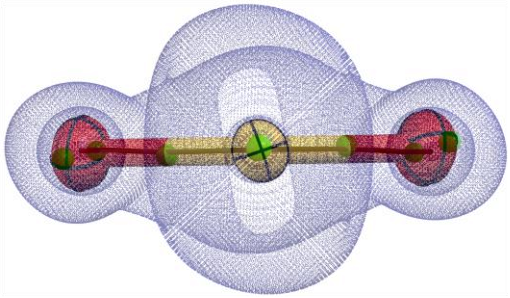
Method	Uxx	Uyy	Uzz	Uxy	Uxz	Uyz
Sulphur						
Tonto (statistical w.s.)	0.01941(4)	0.01643(3)	0.01731(3)	0.00180(4)	0.00000	0.00000
Olex2 (statistical w.s.)	0.01942(4)	0.01644(3)	0.01732(3)	0.00180(4)	0	0
Olex2 (SHELX w.s.)	0.01954(4)	0.01666(4)	0.01747(4)	0.00183(3)	0	0
Olex2 (SHELX w.s. – signal *B*)	0.01952(5)	0.01662(4)	0.01744(4)	0.00184(4)	0	0
Oxygen						
Tonto (statistical w.s.)	0.02399(10)	0.02650(10)	0.03300(11)	0.00475(10)	0.00323(16)	-0.00679(13)
Olex2 (statistical w.s.)	0.02401(10)	0.02650(10)	0.03302(11)	0.00474(10)	0.00321(16)	-0.00675(13)
Olex2 (SHELX w.s.)	0.02398(11)	0.02641(11)	0.03278(14)	0.00470(9)	0.00350(18)	-0.00687(16)
Olex2 (SHELX w.s. – signal *B*)	0.02391(13)	0.02633(14)	0.03279(18)	0.00460(12)	0.00372(19)	-0.0069(2)



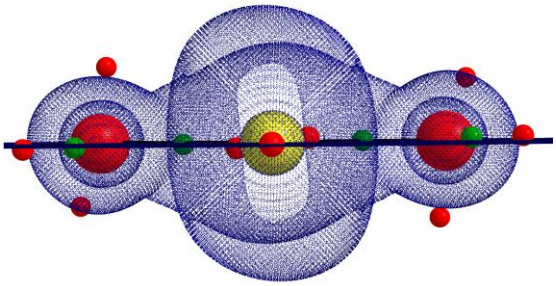
$\mathbf{R}_{full}$



$\mathbf{R}_{full}$ + anharmonicity 4th order (S)



$\mathbf{R}_{full}$ + Thermal ellipsoid (50%)



$\mathbf{R}_{LIST3}$

Figure S5. The (3, +3) and (3, -3) critical points of the Laplacian of the electron density (depicted as green and red points, respectively) of SO_2 for different fittings at $\lambda = 0.360$. The zero surfaces of the Laplacian are shown as blue transparent isosurfaces. The thermal ellipsoid obtained from HAR (middle), drawn at 50% probability level, is superimposed with the zero surface of the Laplacian and its (3, +3) critical points obtained from $\mathbf{R}_{full}$.

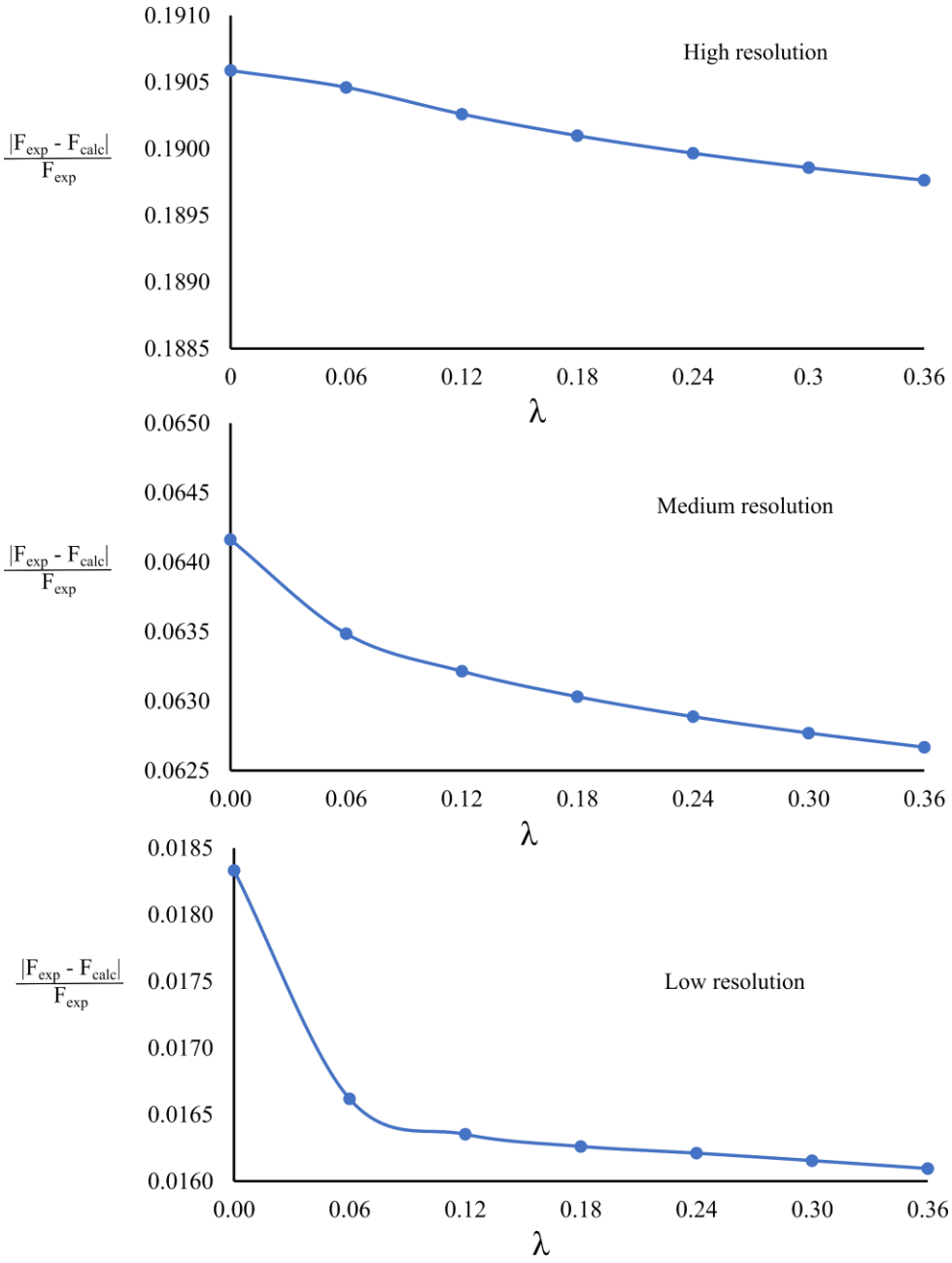


Figure S6. The mean relative error as a function of λ for low, medium and high-resolution intervals. The same intervals are used in the ordinates.

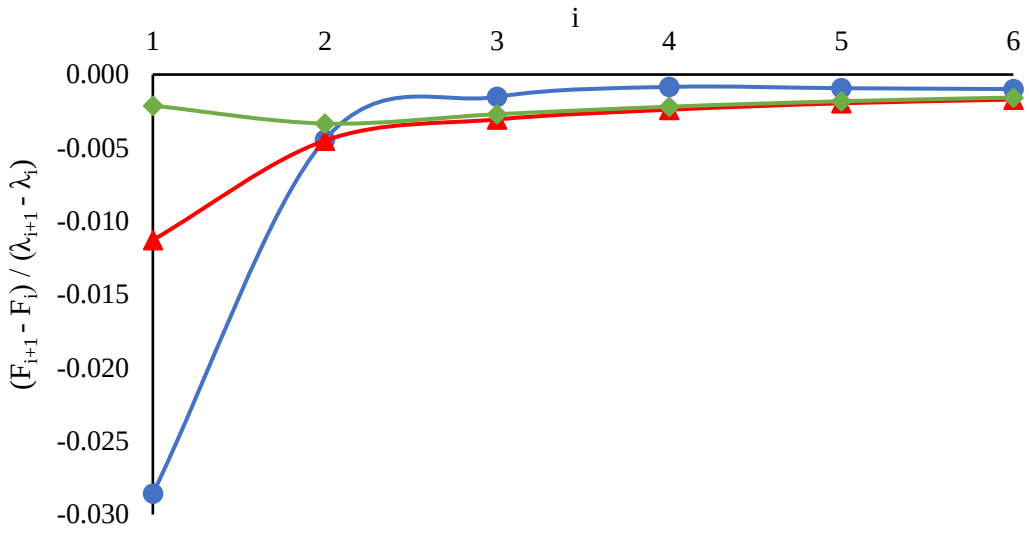


Figure S7. $(F_{i+1} - F_i) / (\lambda_{i+1} - \lambda_i)$ vs. i., where $F_i = |F_{exp(\lambda i)} - F_{calc(\lambda i)}| / F_{exp(\lambda i)}$ (see Figure S5), for low (blue), medium (red) and high (green) resolution intervals.

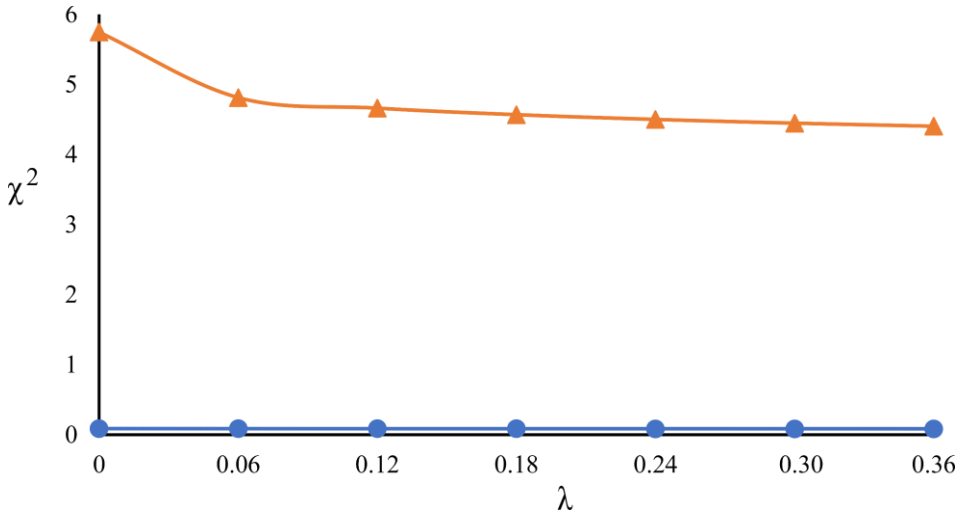


Figure S8. The χ^2 for SO_2 for full data applying the statistical (orange triangles) and unitary (blue circles) weighting schemes, for different λ values.

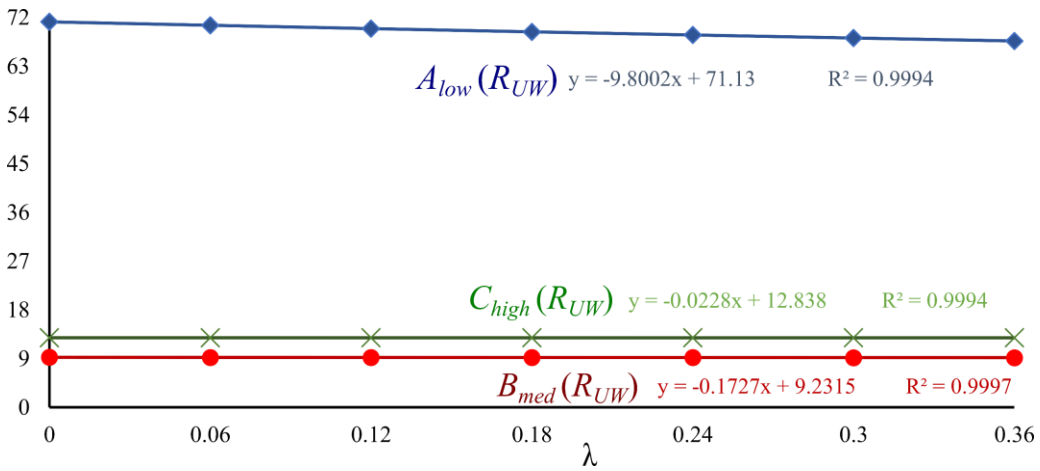


Figure S9. The χ^2decomposition in A_{low}, B_{med} and C_{high} for the full data of SO_2, applying the unitary weighting scheme.

Constrained optimization for three resolution shells: We propose that the fittings (eq. (9)) could be performed progressively: first, the fitting for low-resolution data until convergence. Then, the fitting of medium resolution data until convergence, with the inclusion of the low-resolution data with fixed λ_{max}. Next, the same process is repeated for high-resolution angles with the two previous restrictions fixed. After this cycle is completed, the fitting with low-resolution data will be repeated with the other two restrictions fixed, and so on, until convergence of the three fittings.