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Supporting Information

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Supporting Information for

"Ultrafast Electron Diffraction Reveals Dark Structures of the Biological Chromophore Indole"

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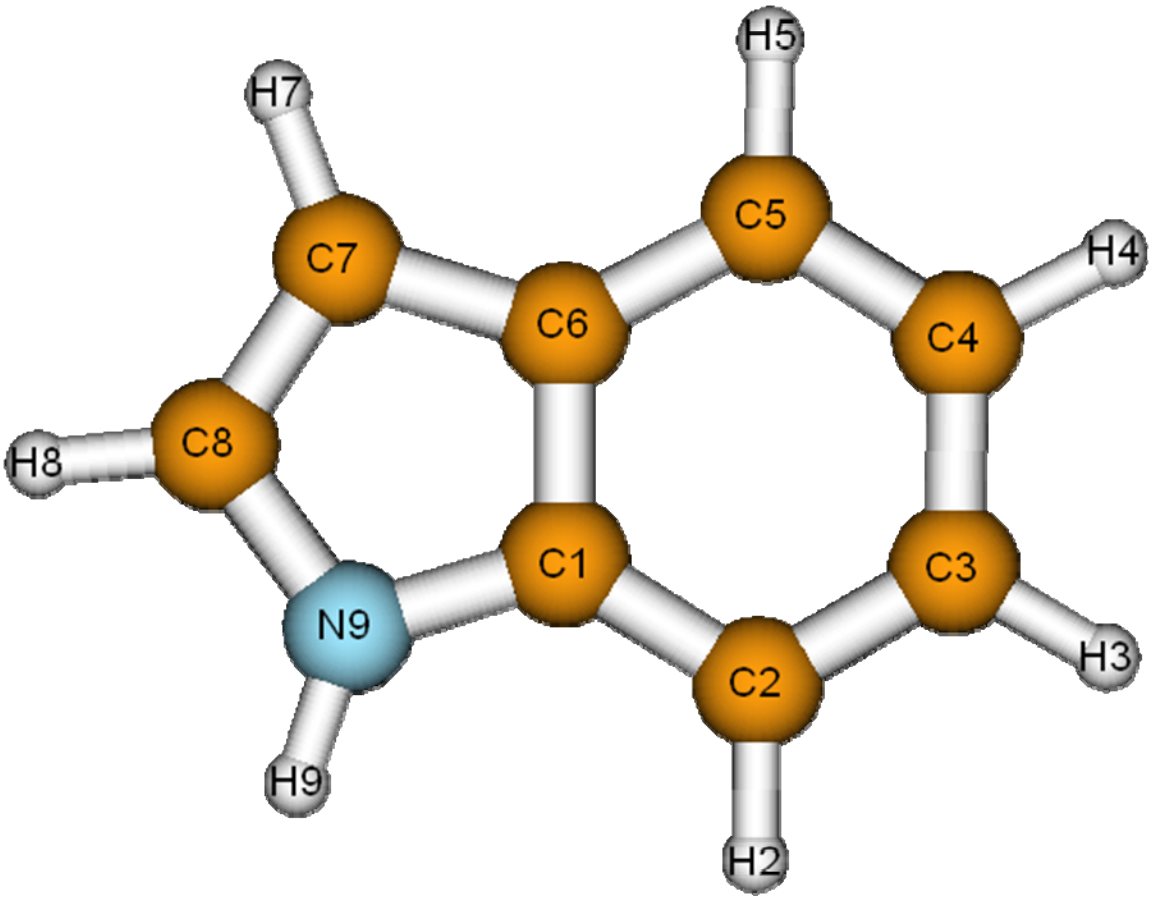


Scheme SI1. The geometry and atomic numbering of the indole molecule.

Table SI1. Structural parameters of indole in the S_0 state.

	UED[a]	DFT
C1-C2	1.404 ± 0.004	1.397
C2-C3	1.392 ± 0.004	1.387
C3-C4	1.414 ± 0.004	1.408
C4-C5	1.391 ± 0.004	1.386
C5-C6	1.406 ± 0.006	1.404
C6-C1	1.428 ± 0.004	1.422
C6-C7	1.438 ± 0.006	1.436
C7-C8	1.376 ± 0.004	1.367
C8-N9	1.389 ± 0.001	1.382
N9-C1	1.388 ± 0.005	1.379
C6-C1-C2	122.3 ± 0.1	122.3
C1-C2-C3	117.4 ± 0.2	117.5
C2-C3-C4	121.2 ± 0.1	121.2
C3-C4-C5	121.2 ± 0.1	121.1
C4-C5-C6	119.0 ± 0.2	119.1
C5-C6-C1	118.8 ± 0.1	118.7
C1-C6-C7	107.0 ± 0.2	106.9
C6-C7-C8	107.2 ± 0.1	107.1
C7-C8-N9	109.5 ± 0.2	109.5
C8-N9-C1	109.2 ± 0.1	109.3
N9-C1-C6	107.1 ± 0.1	107.2
H2-C2		1.085
H3-C3		1.084
H4-C4		1.084
H5-C5		1.085
H7-C7		1.079
H8-C8		1.079
H9-N9		1.005
H2-C2-C1 – H2-C2-C3		0.3
H3-C3-C2 – H3-C3-C4		0.0
H4-C4-C3 – H4-C4-C5		-0.5
H5-C5-C4 – H5-C5-C3		0.2
H7-C7-C6 – H7-C7-C8		1.2
H8-C8-C7 – H8-C8-N9		9.6
H9-N9-C1 – H9-N9-C8		0.3

[a] Five general coordinates out of 10 bond lengths and 11 bending angles were fitted

Table SI1. (continued)

	UED	DFT
C6-C1-C2-C3		0.0
C1-C2-C3-C4		0.0
C2-C3-C4-C5		0.0
C3-C4-C5-C6		0.0
C4-C5-C6-C1		0.0
C5-C6-C1-C2		0.0
C6-C7-C8-N9		0.0
C7-C8-N9-C1		0.0
C8-N9-C1-C6		0.0
N9-C1-C6-C7		0.0
C1-C6-C7-C8		0.0
C4-C5-C6-C7		180.0
C5-C6-C7-C8		180.0
N9-C1-C2-C3		180.0
C8-N9-C1-C2		180.0
C2-C1-C6-C7		180.0
C5-C6-C1-N9		180.0
H2-C2-C1-C3		180.0
H3-C3-C2-C4		180.0
H4-C4-C3-C5		180.0
H5-C5-C4-C3		180.0
H7-C7-C6-C8		180.0
H8-C8-C7-N9		180.0
H9-N9-C1-C8		180.0

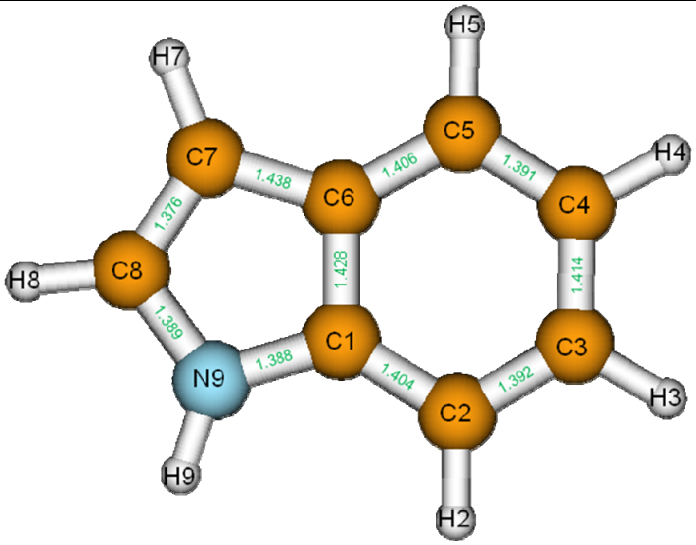


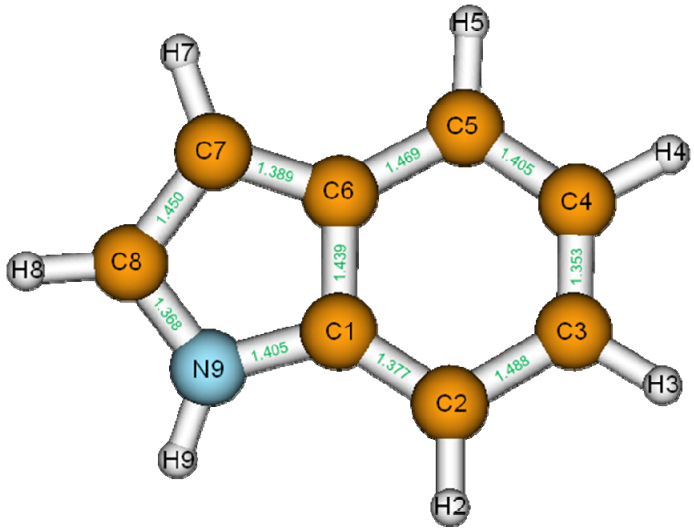
Table SI2. Structural parameters of indole in the T_1 state.

	UED[a]	DFT
C1-C2	1.377 ± 0.039	1.376
C2-C3	1.488 ± 0.036	1.483
C3-C4	1.353 ± 0.032	1.371
C4-C5	1.405 ± 0.044	1.417
C5-C6	1.469 ± 0.034	1.457
C6-C1	1.439 ± 0.040	1.432
C6-C7	1.389 ± 0.021	1.382
C7-C8	1.450 ± 0.015	1.440
C8-N9	1.368 ± 0.013	1.372
N9-C1	1.405 ± 0.024	1.391
C6-C1-C2	122.8 ± 1.3	123.4
C1-C2-C3	116.6 ± 2.1	116.5
C2-C3-C4	121.9 ± 1.7	121.5
C3-C4-C5	122.1 ± 2.0	121.8
C4-C5-C6	118.2 ± 0.9	118.1
C5-C6-C1	118.5 ± 0.6	118.7
C1-C6-C7	107.7 ± 0.7	107.8
C6-C7-C8	108.5 ± 0.5	108.5
C7-C8-N9	106.3 ± 0.9	106.2
C8-N9-C1	111.2 ± 0.5	111.0
N9-C1-C6	106.2 ± 1.7	106.4
H2-C2		1.082
H3-C3		1.083
H4-C4		1.085
H5-C5		1.082
H7-C7		1.080
H8-C8		1.075
H9-N9		1.007
H2-C2-C1 – H2-C2-C3		2.4
H3-C3-C2 – H3-C3-C4		-1.9
H4-C4-C3 – H4-C4-C5		0.4
H5-C5-C4 – H5-C5-C3		0.9
H7-C7-C6 – H7-C7-C8		2.4
H8-C8-C7 – H8-C8-N9		8.7
H9-N9-C1 – H9-N9-C8		-0.6

[a] Four general coordinates out of 10 bond lengths and 11 bending angles were fitted

Table SI2. (continued)

	UED	DFT
C6-C1-C2-C3		0.0
C1-C2-C3-C4		0.0
C2-C3-C4-C5		0.0
C3-C4-C5-C6		0.0
C4-C5-C6-C1		0.0
C5-C6-C1-C2		0.0
C6-C7-C8-N9		0.0
C7-C8-N9-C1		0.0
C8-N9-C1-C6		0.0
N9-C1-C6-C7		0.0
C1-C6-C7-C8		0.0
C4-C5-C6-C7		180.0
C5-C6-C7-C8		180.0
N9-C1-C2-C3		180.0
C8-N9-C1-C2		180.0
C2-C1-C6-C7		180.0
C5-C6-C1-N9		180.0
H2-C2-C1-C3		180.0
H3-C3-C2-C4		180.0
H4-C4-C3-C5		180.0
H5-C5-C4-C3		180.0
H7-C7-C6-C8		180.0
H8-C8-C7-N9		180.0
H9-N9-C1-C8		180.0



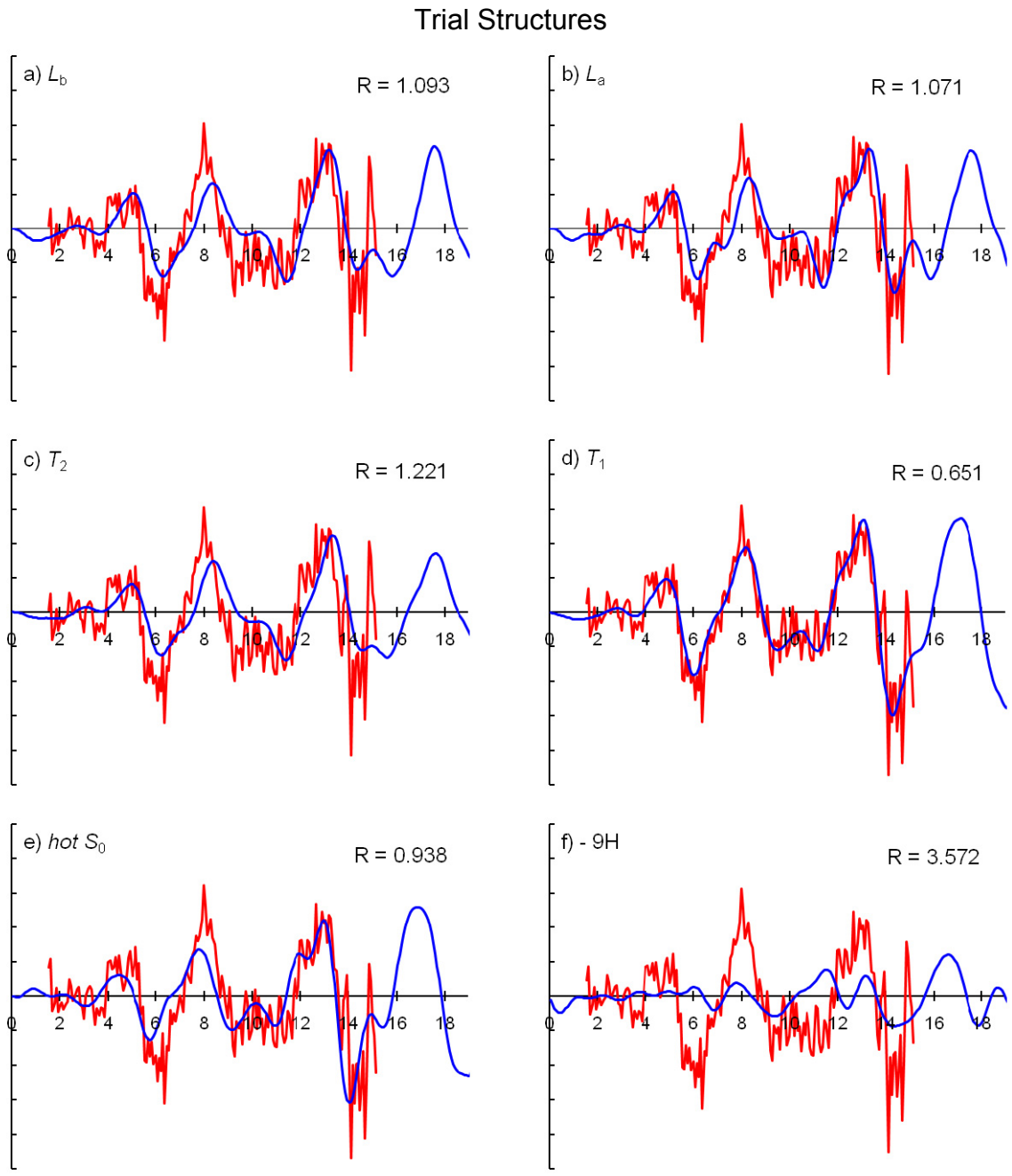


Fig SI1. Temporal frame-referenced molecular scattering function, $\Delta sM(s;\ t = +100$ ps, $t_{ref} = -100$ ps), for trial fits of different reaction pathways of indole. The quality of fit (R value) is also shown for each trial fit. Note that the lower the *R* value (approaching zero) the better the fit, and the T_1 value is the lowest.

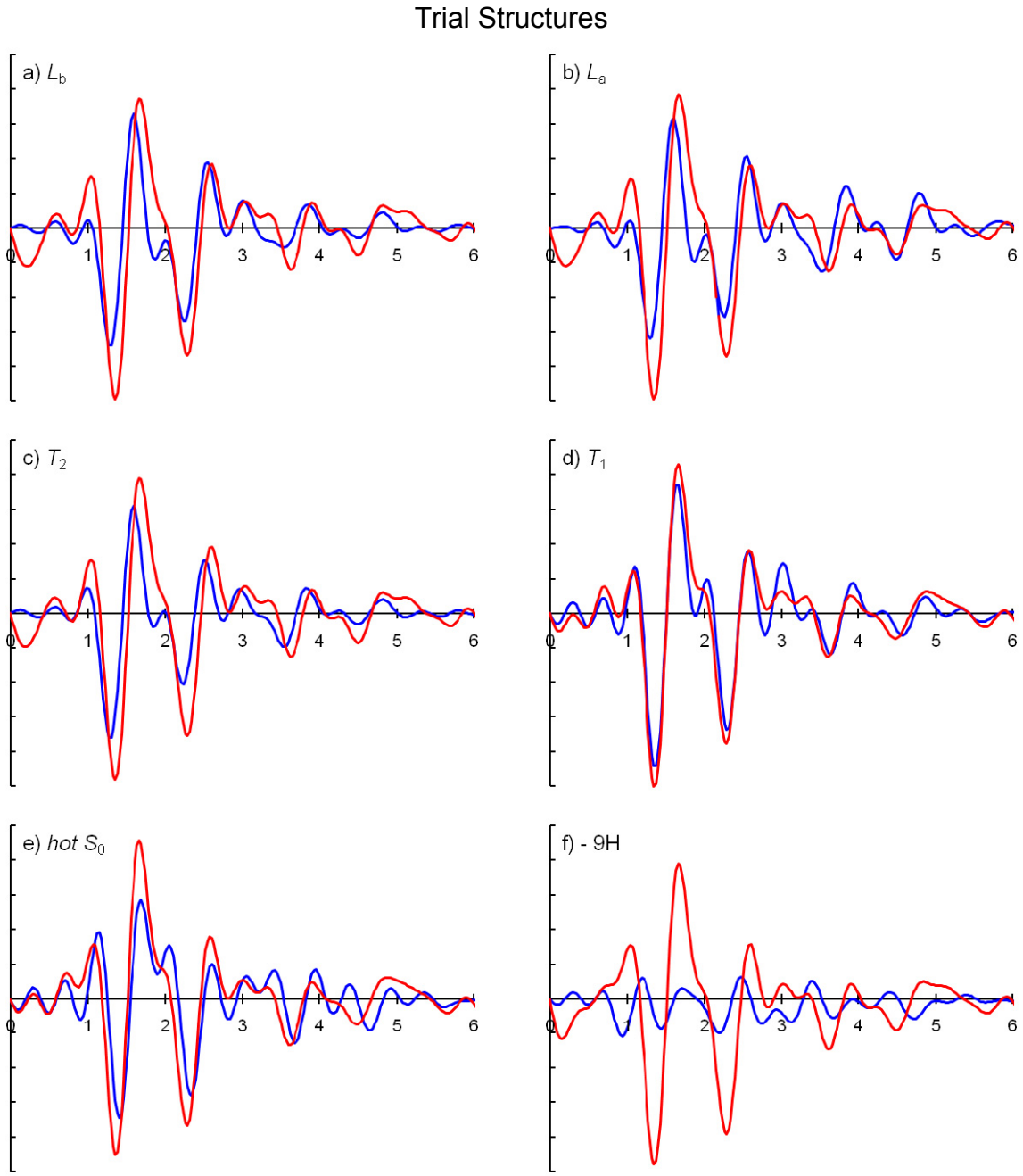


Fig SI2. Temporal frame-referenced radial distribution curves, $\Delta f(r;\ t = +100$ ps, $t_{ref} = -100$ ps), for trial fits of different reaction pathways of indole.

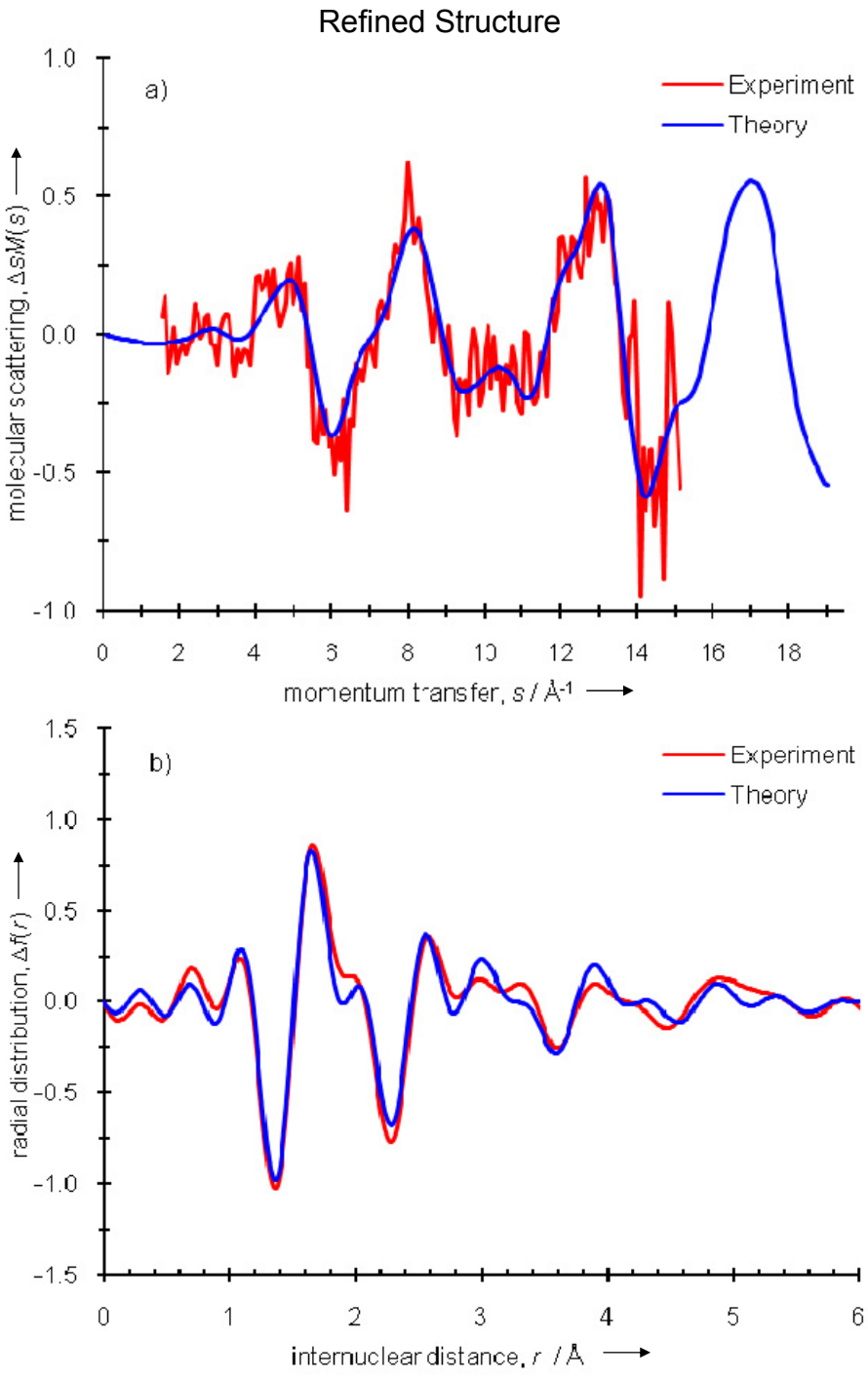


Fig. SI3. The frame-referenced molecular scattering function, $\Delta sM(s)$, and the frame-referenced radial distribution, $\Delta f(r)$, of the indole molecule in the T_1 ($^3\pi\pi^*$) state.