Electronic Supplementary Information for: Retinal shows its true colours: photoisomerization action spectra of mobility-selected isomers of retinal protonated Schiff base

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1 Collision Cross Sections

Eqns. 1 and 2 in the paper can be rearranged to give the flight time through the drift region (t_f), which when added to the ions transit time through the remainder of the machine (t_r), gives the total transit time (t_{tot}).

$$t_{tot} = t_f + t_r = \Omega \frac{16Nl^2}{3ze} \sqrt{\frac{\mu k_B T}{2\pi}} \times \frac{1}{V} + t_r \quad (1)$$

Therefore, Ω, the collision cross section, can be obtained from the slope of the t_{tot} versus $1/V$ plot with the intercept giving the transit time through the remainder of the machine. As an example, such a plot for *trans* RPSB is given in Figure S1.

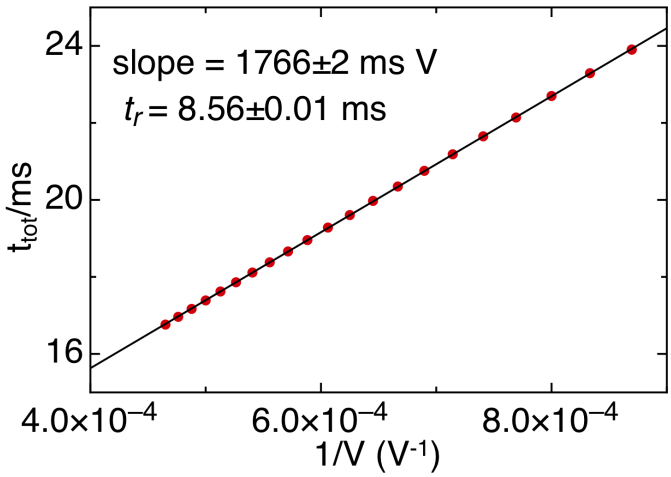

Figure S1: Plot of arrival time (t_{tot}) versus $1/V$ for *trans* RPSB.

2 Arrival Time Distributions

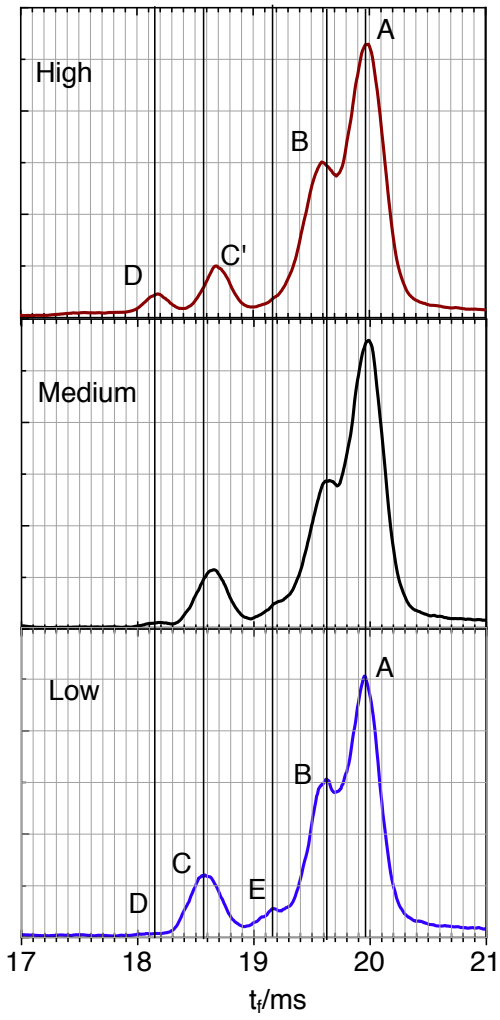

Figure S2: ATDs recorded with IF1 at low, medium and high RF amplitude. In all cases, the sample was irradiated with 468 nm light before electrospray.

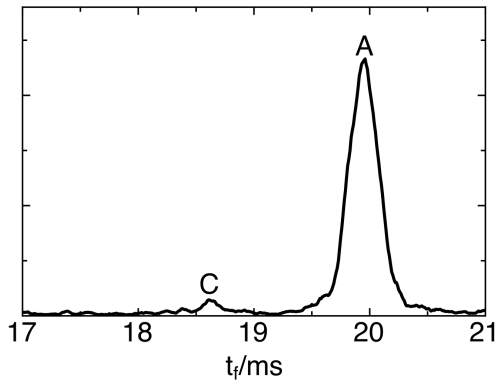

Figure S3: ATD for dark equilibrated RPSB recorded with IF1 at low RF amplitude. The ATD is dominated by the *trans* RPSB peak.

3 PISA Spectra

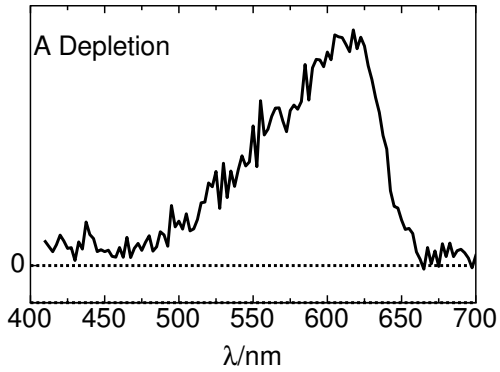

Figure S4: Depletion of isomer A as a function of wavelength. The signal was normalised with respect to photon number.

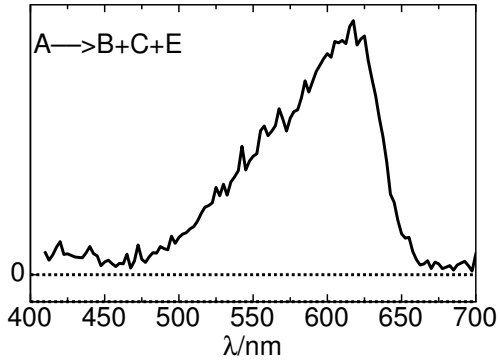

Figure S5: Net formation of isomers B, C, and E from isomer A as a function of wavelength. The signal was normalised with respect to photon number.

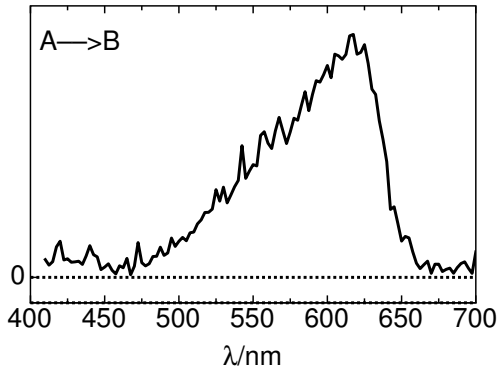

Figure S6: Formation of isomer B from isomer A as a function of wavelength. The signal was normalised with respect to photon number.

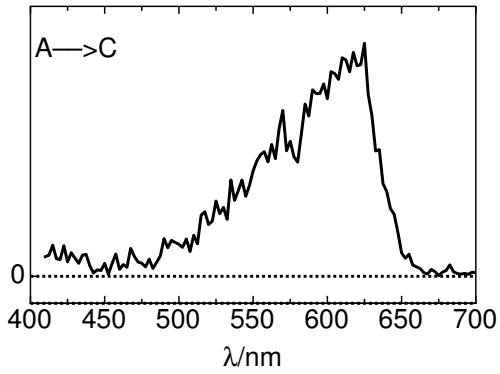

Figure S7: Formation of isomer C from isomer A as a function of wavelength. The signal was normalised with respect to photon number.

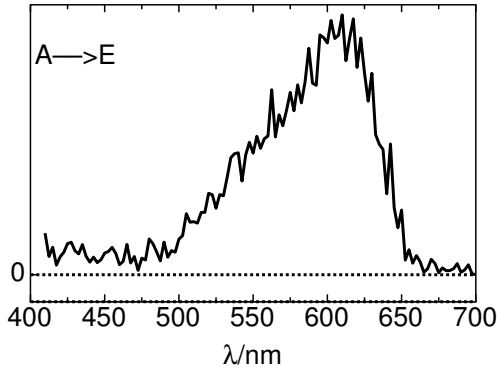

Figure S8: Formation of isomer E from isomer A as a function of wavelength. The signal was normalised with respect to photon number.

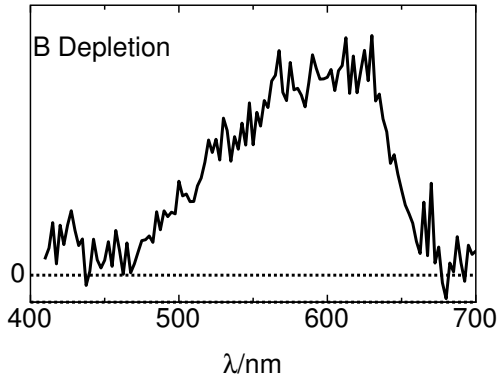

Figure S9: Depletion of isomer B as a function of wavelength. The signal was normalised with respect to photon number.

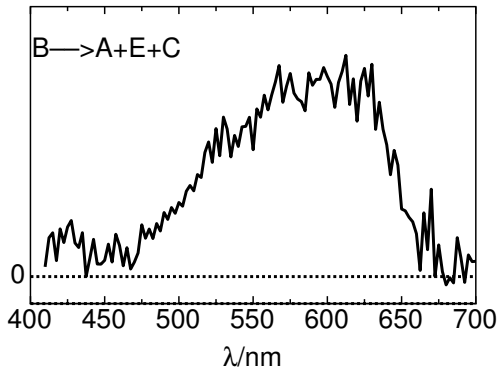

Figure S10: Net formation of isomers A, C, and E from isomer B as a function of wavelength. The signal was normalised with respect to photon number.

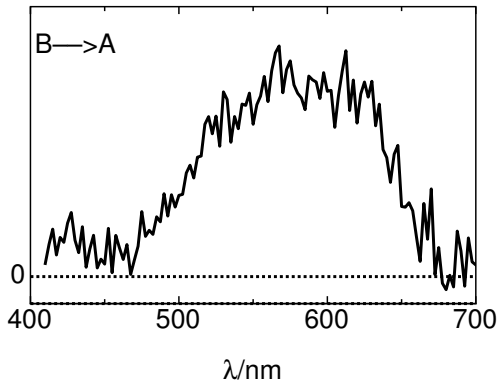

Figure S11: Formation of isomer A from isomer B as a function of wavelength. The signal was normalised with respect to photon number.

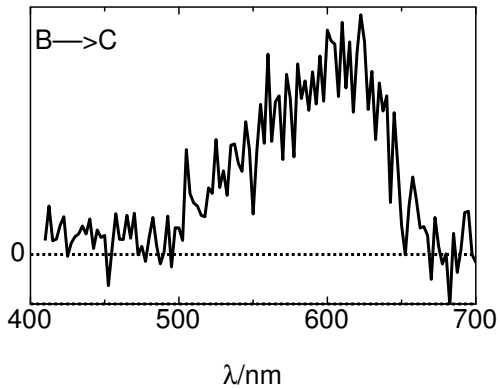

Figure S12: Formation of isomer C from isomer B as a function of wavelength. The signal was normalised with respect to photon number.

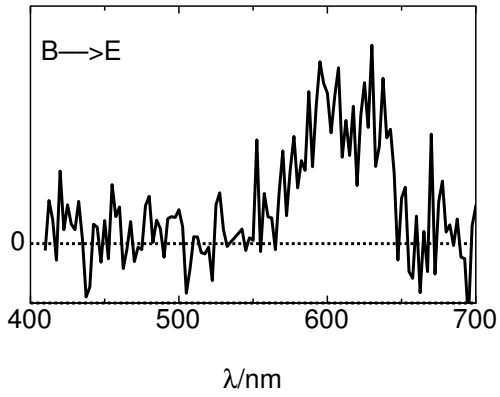

Figure S13: Formation of isomer E from isomer B as a function of wavelength. The signal was normalised with respect to photon number.

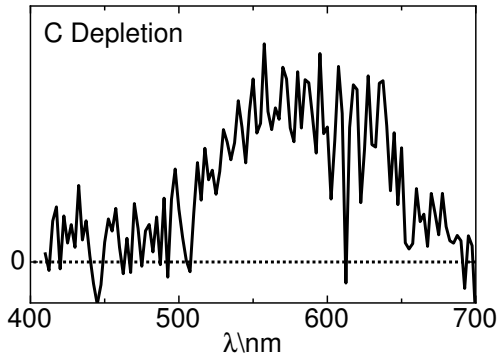

Figure S14: Depletion of isomer C as a function of wavelength. The signal was normalised with respect to photon number.

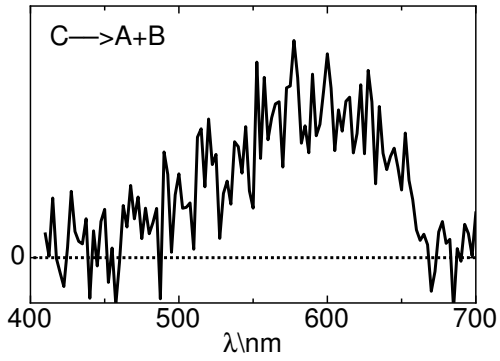

Figure S15: Net formation of isomers A and B from isomer C as a function of wavelength. The signal was normalised with respect to photon number.

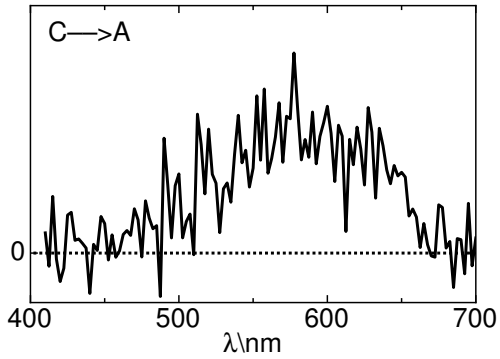

Figure S16: Formation of isomer A from isomer C as a function of wavelength. The signal was normalised with respect to photon number.

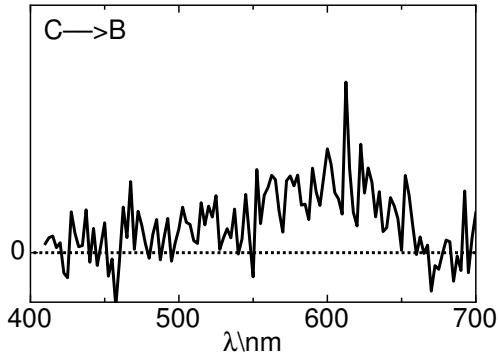

Figure S17: Formation of isomer B from isomer C as a function of wavelength. The signal was normalised with respect to photon number.

4 NMR Spectra

^{1}H spectra were recorded on a Varian Unity Inova 500 spectrometer (499.688 MHz). Samples were were stored in the dark at 0°C prior to analysis.

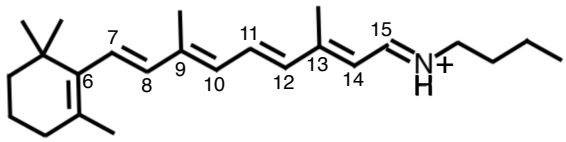

Figure S18: All-*trans* retinal protonated Schiff base.

Table S1: ^{1}H NMR data of neutral N-retinylidene butylamine in CD_3OD.‡

Proton no.	δ (ppm)	multiplicity	J (Hz)
7†	6.16	d	15.6
8†	6.30	d	16.0
10	6.20	d	11.4
11	7.01	dd	14.9, 11.6
12	6.44	d	15.1
14	6.17	d	9.8
15	8.41	d	9.7

† Proton assignments ambiguous
‡ Sovdat et. al., *J. Am. Chem. Soc.*, **134**, 8318-8320, 2012.

Table S2: ^{1}H NMR data of neutral N-retinylidene butylamine in CD_3OD.

Proton no.	δ (ppm)	multiplicity	J (Hz)
7†	6.16	d	14.5
8†	6.30	d	16.0
10	6.20	d	11.5
11	7.01	dd	15.0, 11.5
12	6.44	d	15.0
14	6.17	d	10.5
15	8.41	d	10.0

† Proton assignments ambiguous

Table S3: ^{1}H NMR data for all-*trans* RPSB with a drop of TFA in CD_3OD.‡

Proton no.	δ (ppm)	multiplicity	J (Hz)
7	6.54	d	15.8
8	6.26	d	16.0
10	6.35	d	11.7
11	7.58	dd	14.7, 11.6
12	6.62	d	14.9
14	6.41	d	11.0
15	8.84	d	11.5

‡ Sovdat et. al., *J. Am. Chem. Soc.*, **134**, 8318-8320, 2012.

Table S4: ^{1}H NMR data for all-*trans* RPSB in CD_3OD with 20μL TFA added.

Proton no.	δ (ppm)	multiplicity	J (Hz)
7	6.56	d	16.5
8	6.28	d	16.0
10	6.36	d	11.5
11	7.58	dd	15.0, 12.0
12	6.63	d	15.0
14	6.42	d	11.0
15	8.84	d	11.0

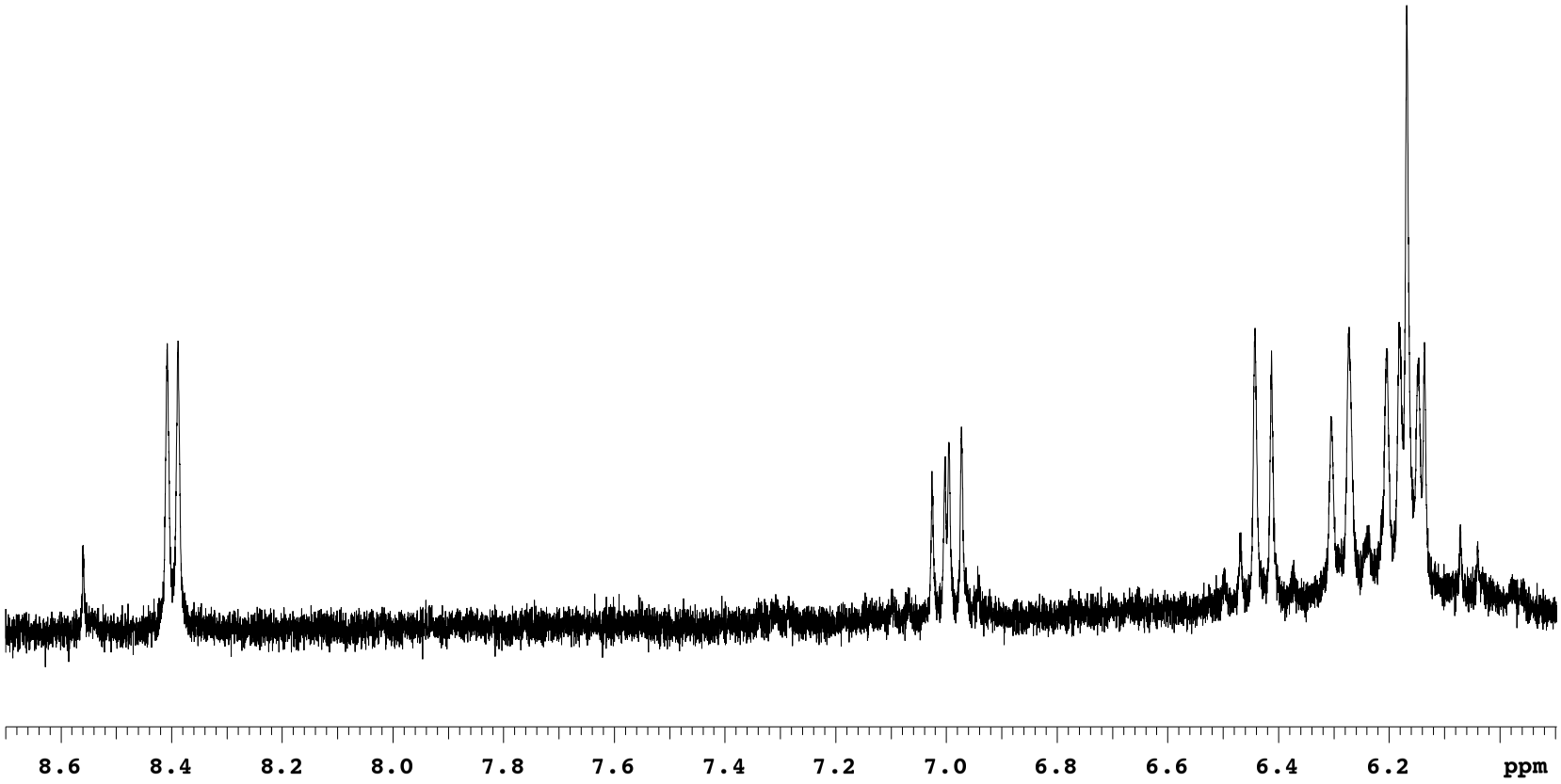

Figure S19: ^{1}H NMR spectrum of RSB in CD_3OD from 6–8.7 ppm

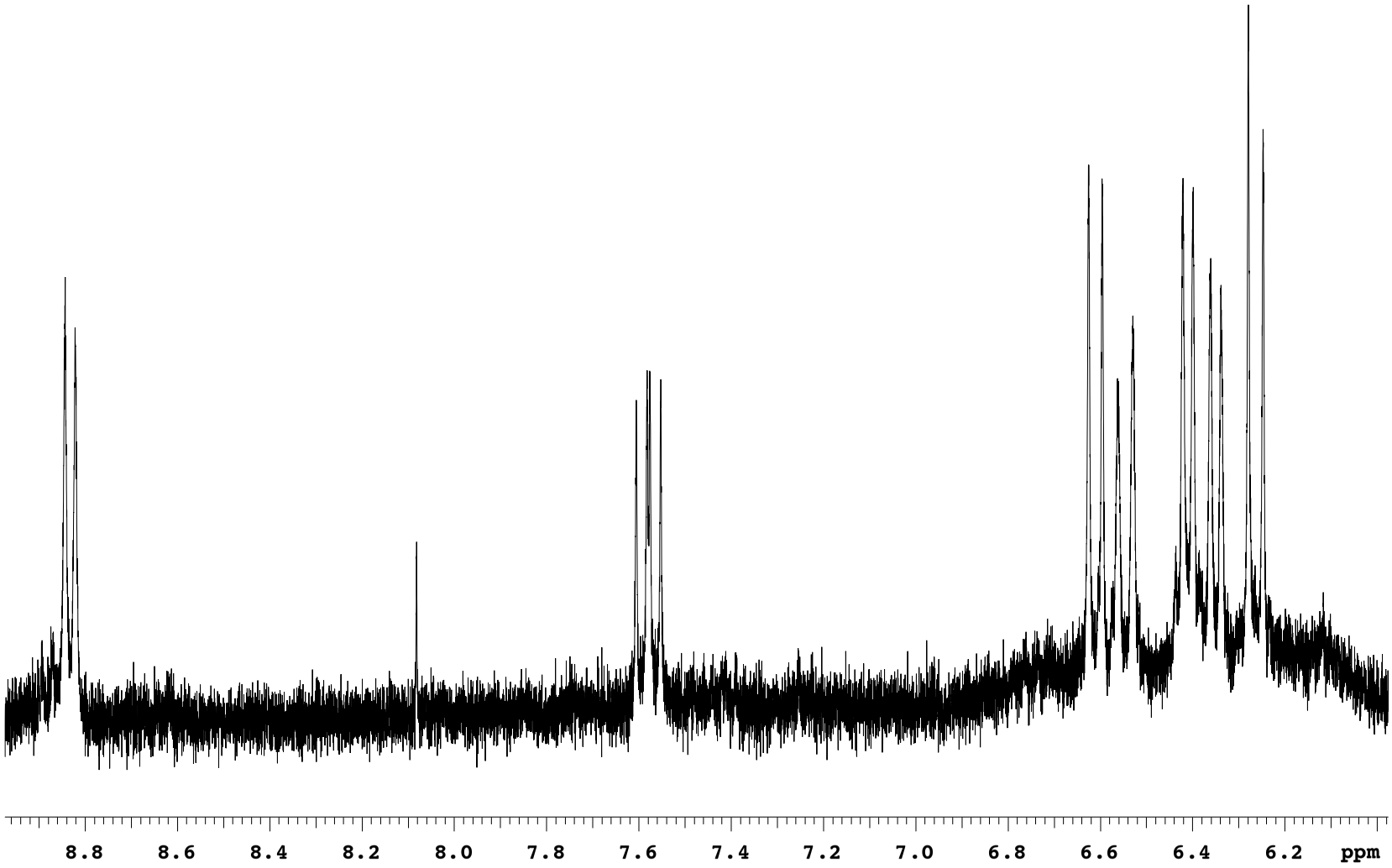

Figure S20: ^{1}H NMR spectrum of RPSB in CD_3OD with 20μL TFA added, from 6–9.0 ppm

5 DFT calculations

The following tables report data for RPSB isomers based on M06- 2X/cc-pVDZ DFT calculations and include relative energies corrected for vibrational zero point energy (ΔE), free energies at T=298.15 K (ΔG), and collision cross sections (Ω_{calc}) determined using the MOBCAL trajectory method from Shvartsburg et al. (*Chem. Phys. Lett.*, **261**, 86, 1996) and Mesleh et al. (*J. Phys. Chem.* **100**, 16082, 1996). Atom-atom interaction parameters for collisions between N_2 and the RPSB were taken from Campuzano et al. (*Anal. Chem.*, **84**, 1026, 2012). The majority of the data are reproduced from Coughlan et. al. (*J. Chem. Phys.*, **140**, 164307, 2014), but have been supplemented by more recent calculations.

The calculated collision cross sections for single-*cis* isomers presented in Table 1 of the paper are averaged over their respective 6s conformations. The average collision cross-section, ($\overline{\Omega}$), for interconverting population of 6s isomers is given by:

$$\overline{\Omega} = \sum_{i=1}^{3} \Omega_i e^{\frac{-\Delta E_i}{RT}} / \sum_{i=1}^{3} e^{\frac{-\Delta E_i}{RT}} \tag{2}$$

where the sum is over the 6s-*cis*(-), 6s-*cis*(+) and 6s-*trans* isomers, and in each case ΔE_i is the relative energy corrected for vibrational zero point energy at T=298.15 K (close to the effective temperature in the drift region).

Table S5: Calculated energies relative to the 6s-*cis*(-) isomer and trajectory method collision cross sections (Ω_{calc}) for all-*trans* and single-*cis* isomers of RPSB.

isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
6s-*cis*(-)	0	0	220.6
6s-*cis*(+)	2.3	4.8	220.1
6s-*trans*	0.7	7.1	218.8
7-*cis*, 6s-*cis*(-)	13.2	14.4	216.0
7-*cis*, 6s-(+)	15.5	16.7	215.1
7-*cis*, 6s-*trans*	61.1	58.7	216.3
8-*cis*, 6s-*cis*(-)	11.4	10.8	220.9
8-*cis*, 6s-*cis*(+)	12.5	10.4	214.0
8-*cis*, 6s-*trans*	13.6	11.6	219.5
9-*cis*, 6s-*cis*(-)	6.0	8.3	217.4
9-*cis*, 6s-*cis*(+)	8.3	7.6	219.2
9-*cis*, 6s-*trans*	6.5	7.5	214.2
10-*cis*, 6s-*cis*(-)	23.6	27.1	218.3
10-*cis*, 6s-*cis*(+)	23.7	24.8	218.7
10-*cis*, 6s-*trans*	23.5	23.4	217.0
11-*cis*, 6s-*cis*(-)	20.2	15.9	218.6
11-*cis*, 6s-*cis*(+)	23.9	24.3	218.3
11-*cis*, 6s-*trans*	22.6	24.0	214.7
12-*cis*, 6s-*cis*(-)	10.7	14.2	219.9
12-*cis*, 6s-*cis*(+)	10.8	7.7	220.9
12-*cis*, 6s-*trans*	9.7	3.5	220.1
13-*cis*, 6s-*cis*(-)	5.5	3.8	219.9
13-*cis*, 6s-*cis*(+)	9.3	12.4	219.7
13-*cis*, 6s-*trans*	7.3	9.7	217.5

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isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
14-*cis*, 6s-*cis*(-)	17.9	19.8	219.1
14-*cis*, 6s-*cis*(+)	18.1	20.3	219.5
14-*cis*, 6s-*trans*	18.0	20.4	218.6
15-*cis*, 6s-*cis*(-)	2.4	6.6	217.9
15-*cis*, 6s-*cis*(+)	4.5	7.4	218.2
15-*cis*, 6s-*trans*	4.1	8.7	215.8

Table S6: Calculated energies relative to the 6s-*cis*(-) isomer and trajectory method collision cross sections (Ω_{calc}) for double-*cis* isomers of RPSB. Due to steric crowding, some 7-*cis* isomers are unstable [indicated by a star (⋆)].

isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
7, 8-*cis*, 6s-*cis*(-)	17.5	19.9	214.8
7, 8-*cis*, 6s-*cis*(+)	19.8	21.5	215.9
7, 8-*cis*, 6s-*trans*	28.4	32.9	203.4
7,9-*cis*, 6s-*cis*(-)	19.5	24.7	216.9
7, 9-*cis*, 6s-*cis*(+)	17.0	20.9	215.1
7, 9-*cis*, 6s-*trans*⋆			
7, 10-*cis*, 6s-*cis*(-)	32.7	36.4	214.1
7, 10-*cis*, 6s-*cis*(+)	35.9	42.0	214.6
7, 10-*cis*, 6s-*trans*⋆			
7, 11-*cis*, 6s-*cis*(-)	35.5	40.1	212.0
7, 11-*cis*, 6s-*cis*(+)	37.0	43.8	213.6
7, 11-*cis*, 6s-*trans*	101.8	102.2	212.9
7, 12-*cis*, 6s-*cis*(-)	25.6	29.3	214.2
7, 12-*cis*, 6s-*cis*(+)	37.0	43.8	215.1
7, 12-*cis*, 6s-*trans*⋆			
7, 13-*cis*, 6s-*cis*(-)	21.6	27.0	216.6
7, 13-*cis*, 6s-*cis*(+)	19.7	25.0	215.9
7, 13-*cis*, 6s-*trans*	21.9	25.8	215.7
7, 14-*cis*, 6s-*cis*(-)	32.2	38.2	212.2
7, 14-*cis*, 6s-*cis*(+)	31.4	31.1	214.3
7, 14-*cis*, 6s-*trans*	100.9	106.2	212.9
7, 15-*cis*, 6s-*cis*(-)	16.7	23.6	214.4
7, 15-*cis*, 6s-*cis*(+)⋆			
7, 15-*cis*, 6s-*trans*	81.3	84.3	211.0
8, 9-*cis*, 6s-*cis*(-)	10.0	9.1	214.3
8, 9-*cis*, 6s-*cis*(+)	11.0	7.8	214.7
8, 9-*cis*, 6s-*trans*	17.4	18.4	211.9
8, 10-*cis*, 6s-*cis*(-)	29.7	28.4	221.3
8, 10-*cis*, 6s-*cis*(+)	32.1	34.4	219.8
8, 10-*cis*, 6s-*trans*	31.1	31.0	217.6
8, 11-*cis*, 6s-*cis*(-)	32.8	37.1	217.7
8, 11-*cis*, 6s-*cis*(+)	33.2	34.2	216.4

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isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
8, 11-*cis*, 6s-*trans*	36.3	34.8	214.6
8, 12-*cis*, 6s-*cis*(-)	21.8	19.8	223.8
8, 12-*cis*, 6s-*cis*(+)	22.7	23.4	223.2
8, 12-*cis*, 6s-*trans*	21.8	19.4	221.0
8, 13-*cis*, 6s-*cis*(-)	16.1	15.4	218.1
8, 13-*cis*, 6s-*cis*(+)	20.2	22.0	216.5
8, 13-*cis*, 6s-*trans*	19.9	16.9	215.9
8, 14-*cis*, 6s-*cis*(-)	28.3	29.6	220.9
8, 14-*cis*, 6s-*cis*(+)	29.9	32.6	219.7
8, 14-*cis*, 6s-*trans*	29.3	27.3	217.2
8, 15-*cis*, 6s-*cis*(-)	11.2	13.2	217.7
8, 15-*cis*, 6s-*cis*(+)	12.8	14.1	218.1
8, 15-*cis*, 6s-*trans*	13.8	15.5	217.6
9, 10-*cis*, 6s-*cis*(-)	23.8	27.7	211.7
9, 10-*cis*, 6s-*cis*(+)	26.4	28.0	214.0
9, 10-*cis*, 6s-*trans*	25.1	26.1	209.9
9, 11-*cis*, 6s-*cis*(-)	26.8	27.8	219.4
9, 11-*cis*, 6s-*cis*(+)	26.0	25.8	218.7
9, 11-*cis*, 6s-*trans*	26.3	25.3	217.0
9, 12-*cis*, 6s-*cis*(-)	16.8	17.7	215.9
9, 12-*cis*, 6s-*cis*(+)	16.0	14.4	217.3
9, 12-*cis*, 6s-*trans*	18.2	20.2	212.0
9, 13-*cis*, 6s-*cis*(-)	8.3	10.2	219.5
9, 13-*cis*, 6s-*cis*(+)	10.0	13.0	218.9
9, 13-*cis*, 6s-*trans*	10.6	10.8	215.2
9, 14-*cis*, 6s-*cis*(-)	22.2	24.8	215.1
9, 14-*cis*, 6s-*cis*(+)	22.0	13.8	216.2
9, 14-*cis*, 6s-*trans*	22.1	23.2	211.8
9, 15-*cis*, 6s-*cis*(-)	4.5	6.1	215.9
9, 15-*cis*, 6s-*cis*(+)	4.9	5.2	218.1
9, 15-*cis*, 6s-*trans*	4.2	5.6	213.0
10, 11-*cis*, 6s-*cis*(-)	44.6	47.1	215.1
10, 11-*cis*, 6s-*cis*(+)	47.8	53.5	213.7
10, 11-*cis*, 6s-*trans*	45.2	46.1	212.6
10, 12-*cis*, 6s-*cis*(-)	29.5	25.6	220.1
10, 12-*cis*, 6s-*cis*(+)	31.5	26.9	220.4
10, 12-*cis*, 6s-*trans*	29.3	24.6	217.4
10, 13-*cis*, 6s-*cis*(-)	30.1	33.1	216.6
10, 13-*cis*, 6s-*cis*(+)	31.4	32.5	216.1
10, 13-*cis*, 6s-*trans*	32.0	33.0	214.6
10, 14-*cis*, 6s-*cis*(-)	39.5	43.3	216.8
10, 14-*cis*, 6s-*cis*(+)	40.0	37.9	217.7
10, 14-*cis*, 6s-*trans*	39.4	36.6	215.7
10, 15-*cis*, 6s-*cis*(-)	22.3	25.6	216.2
10, 15-*cis*, 6s-*cis*(+)	23.3	24.9	216.9
10, 15-*cis*, 6s-*trans*	23.4	24.7	215.1
11, 12-*cis*, 6s-*cis*(-)	32.0	33.6	215.7
11, 12-*cis*, 6s-*cis*(+)	31.5	27.4	213.6

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isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
11, 12-*cis*, 6s-*trans*	29.7	30.2	212.6
11, 13-*cis*, 6s-*cis*(-)	27.1	28.5	219.2
11, 13-*cis*, 6s-*cis*(+)	28.5	28.0	218.1
11, 13-*cis*, 6s-*trans*	28.3	31.5	216.2
11, 14-*cis*, 6s-*cis*(-)	41.2	43.4	215.7
11, 14-*cis*, 6s-*cis*(+)	41.6	42.4	215.4
11, 14-*cis*, 6s-*trans*	40.5	36.1	211.5
11, 15-*cis*, 6s-*cis*(-)	21.6	23.4	216.9
11, 15-*cis*, 6s-*cis*(+)	22.6	24.0	217.6
11, 15-*cis*, 6s-*trans*	22.2	23.7	214.3
12, 13-*cis*, 6s-*cis*(-)	15.8	15.2	216.5
12, 13-*cis*, 6s-*cis*(+)	20.7	24.9	216.9
12, 13-*cis*, 6s-*trans*	17.8	19.3	216.5
12, 14-*cis*, 6s-*cis*(-)	25.6	29.8	218.7
12, 14-*cis*, 6s-*cis*(+)	24.2	24.3	217.5
12, 14-*cis*, 6s-*trans*	24.0	26.5	216.7
12, 15-*cis*, 6s-*cis*(-)	11.5	14.3	215.7
12, 15-*cis*, 6s-*cis*(+)	10.1	6.6	215.9
12, 15-*cis*, 6s-*trans*	9.8	8.9	215.9
13, 14-*cis*, 6s-*cis*(-)	23.8	27.8	216.5
13, 14-*cis*, 6s-*cis*(+)	23.5	25.2	215.8
13, 14-*cis*, 6s-*trans*	22.9	25.3	214.2
13, 15-*cis*, 6s-*cis*(-)	5.8	6.7	219.2
13, 15-*cis*, 6s-*cis*(+)	8.4	12.3	219.1
13, 15-*cis*, 6s-*trans*	7.7	11.0	217.1
14, 15-*cis*, 6s-*cis*(-)	33.4	39.9	216.4
14, 15-*cis*, 6s-*cis*(+)	34.8	38.2	217.4
14, 15-*cis*, 6s-*trans*	34.3	37.3	216.2

Table S7: Calculated energies relative to the 6s-*cis*(-) isomer and trajectory method collision cross sections (Ω_{calc}) for sequential triple-*cis* isomers of RPSB. Due to steric crowding, some 7-*cis* isomers are unstable [indicated by a star (⋆)].

isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
7, 8, 9-*cis*, 6s-*cis*(-)	22.0	29.3	203.7
7, 8, 9-*cis*, 6s-*cis*(+)	23.4	30.8	204.4
7, 8, 9-*cis*, 6s-*trans*⋆			
8, 9, 10-*cis*, 6s-*cis*(-)	39.1	41.4	209.6
8, 9, 10-*cis*, 6s-*cis*(+)	42.4	49.5	209.1
8, 9, 10-*cis*, 6s-*trans*	44.0	46.4	206.2
9, 10, 11-*cis*, 6s-*cis*(-)	39.9	49.7	201.0
9, 10, 11-*cis*, 6s-*cis*(+)	39.8	43.5	203.0
9, 10, 11-*cis*, 6s-*trans*	39.0	46.4	204.3
10, 11, 12-*cis*, 6s-*cis*(-)	48.1	51.1	211.0
10, 11, 12-*cis*, 6s-*cis*(+)	44.4	51.6	201.2
10, 11, 12-*cis*, 6s-*trans*	49.4	48.1	210.7

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isomer	ΔE kJ/mol	ΔG kJ/mol	Ω_{calc} Å^2
11, 12, 13-*cis*, 6s-*cis*(-)	30.0	31.2	210.0
11, 12, 13-*cis*, 6s-*cis*(+)	24.4	32.2	196.3
11, 12, 13-*cis*, 6s-*trans*	33.0	34.7	209.0
12, 13, 14-*cis*, 6s-*cis*(-)	33.3	38.1	202.3
12, 13, 14-*cis*, 6s-*cis*(+)	33.9	36.6	205.0
12, 13, 14-*cis*, 6s-*trans*	35.2	39.3	202.8
13, 14, 15-*cis*, 6s-*cis*(-)	36.9	43.8	205.7
13, 14, 15-*cis*, 6s-*cis*(+)	37.5	46.2	202.2
13, 14, 15-*cis*, 6s-*trans*	37.8	46.7	200.4