Supplementary Information: Electronic Spectroscopy of Cryogenic Protonated Schiff-base Retinal Derivatives

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Fragment Mass Analysis

Fragment masses can be produced and stored in the electrostatic storage ring SAPHRIRA, as explained in the main article, by irradiating ions trapped in the cryogenically cooled radio-frequency (RF) ion trap. The hot ground-state ions are fragmented, and both parent ions and fragments are stored and cooled in the RF-ion trap. By applying the full storage voltage to the first corner in SAPHIRA, the ring closes, and the ion beam is dumped onto the delayed MCP detector. The time-of-flight of the ions can be turned into a mass-to-charge ratio as shown in panel b og Fig. S1. One can use this information to calculate the separation time for different masses and open the second corner appropriately to clean the beam to the desired mass. Doing this typically requires a bit higher resolution, which can be gained by looking at the Fourier transform of the trapped beam. Using OH^- as a reference with 17.87949 μs revolution time[1], it is possible to get a mass-to-charge ratio from the different revolution times. However, this spectrum is full of harmonics of all masses present. In order to get rid of them, we perform a comb search of harmomics for each mass m,

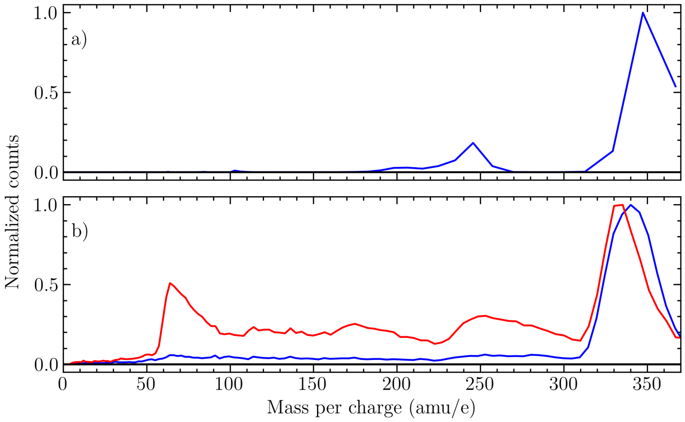

Figure S1 Top: Fourier transforms of the delayed detector signal from circulating ions in SAPHIRA upon irradiating RPSB at 596 nm in the cryogenic RF-ion trap. A harmonic comb search has been run through the Fourier trace to remove harmonic masses. Bottom: Mass-to-charge ratio measured by the difference in time-of-flight from the cryogenic RF-ion trap to arrival on the delayed MCP detector after one revolution in SAPHIRA. Curves are shown with (red) and without (blue) laser irradiation of RPSB.

$$S(m) = \sum_i A_i \left(\frac{1 - \Delta f_i}{\Delta f_p / 2} \right)^n = \sum_i S_i, \tag{S1}$$

where A_i is the amplitude of the closest peak to the i'th harmonic of mass m, Δf_i the distance to that peak and Δf_p the distance between the two peaks within the i'th harmonic lies. Fig. S2 illustrates equation S1. Given a chosen regularisation constant n, one can get a cleaner mass-to-charge spectrum. However, the comb search fixes most harmonic problems; it does not fix the fact that higher-harmonic peaks of one mass can be mistaken for the first harmonic of other masses. One can further constrain the Fourier mass-to-charge ratio transform by introducing a conditional loss function,

$$S_i^* = S_{i+1} \left(\frac{S_i}{S_i + S_i + 1} \right)^k, \quad S_{i+1} + \Delta_{tol} > S_i. \tag{S2}$$

A chosen regularisation constant k and tolerance Δ_{tol} must be set. In Fig. S1 $n = k = 8$ and the comb search sum is truncated at $i = 11$. The tolerance is set to an arbitrary 50%.

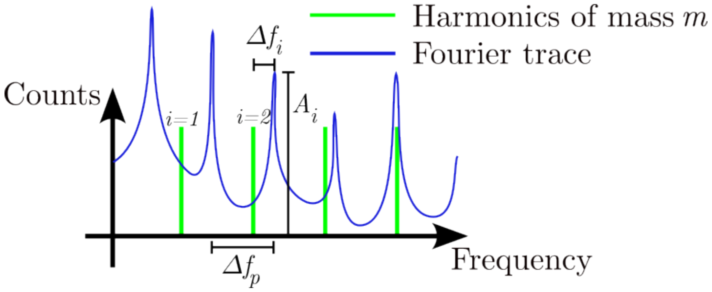

Figure S2 Depiction of equation S1 with a Fourier trace in blue and the first four harmonics of a mass m. The variables in equation S1 are depicted for the second harmonic $i = 2$

Particle-in-a-box Model

Andersen et al.[2] demonstrated that a simple particle-in-a-box model provides an intuitive explanation for the absorption characteristics of the retinal protonated Schiff-base. Using this analogy, we can consider electrons in a one-dimensional infinite potential well with energy given by,

$$E_n = n^2 \frac{h^2}{8m_e L^2}. \tag{S3}$$

Here, m_e denotes the electron mass and L represents the length of the box. The retinal system can be modelled as an infinite potential well extending from the lone methyl group on the ring to the nitrogen atom, with 12 electrons occupying the well. Using an average bond distance of 130 pm, excitation from the highest occupied level (6) to the first excited level (7) results in an energy difference of $E_7 - E_6 = 617$ nm. Similarly, when the system is contracted by two bond lengths and contains two fewer electrons, the energy difference $E_6 - E_5 = 506$ nm. Although this model is highly simplified, the observed trend closely aligns with experimental measurements.

Table of Energies

A summary of the features found in the action-absorption spectra is given in table 1.

Name	Fig. 3 panel	Cooled Features (nm)	Room Temp. Features (nm)
RPSB	a	595.7	620
No β-ionone ring	b	593.3, 590.1, 573.5	600
$C_6 = C_7$ *trans*-locked	c		614
$C_9 = C_{10}$ *trans*-locked	d	590	600
Ring N-dimethylated	e	600	
Ring methylated	f	525	
$C_6 = C_7$ *cis*-locked	g	512,4, 537.6, 554.5	

Table 1 Table of prominent features and absorption maxima found in Figure 3, for the different analogues studied.

References

[1] H. B. Pedersen, H. Juul, F. K. Mikkelsen, A. P. Rasmussen and L. H. Andersen, *Physical Review A*, 2022, **106**, 053111.

[2] L. H. Andersen and A. Bochenkova, *The European Physical Journal D*, 2009, **51**, 5–14.