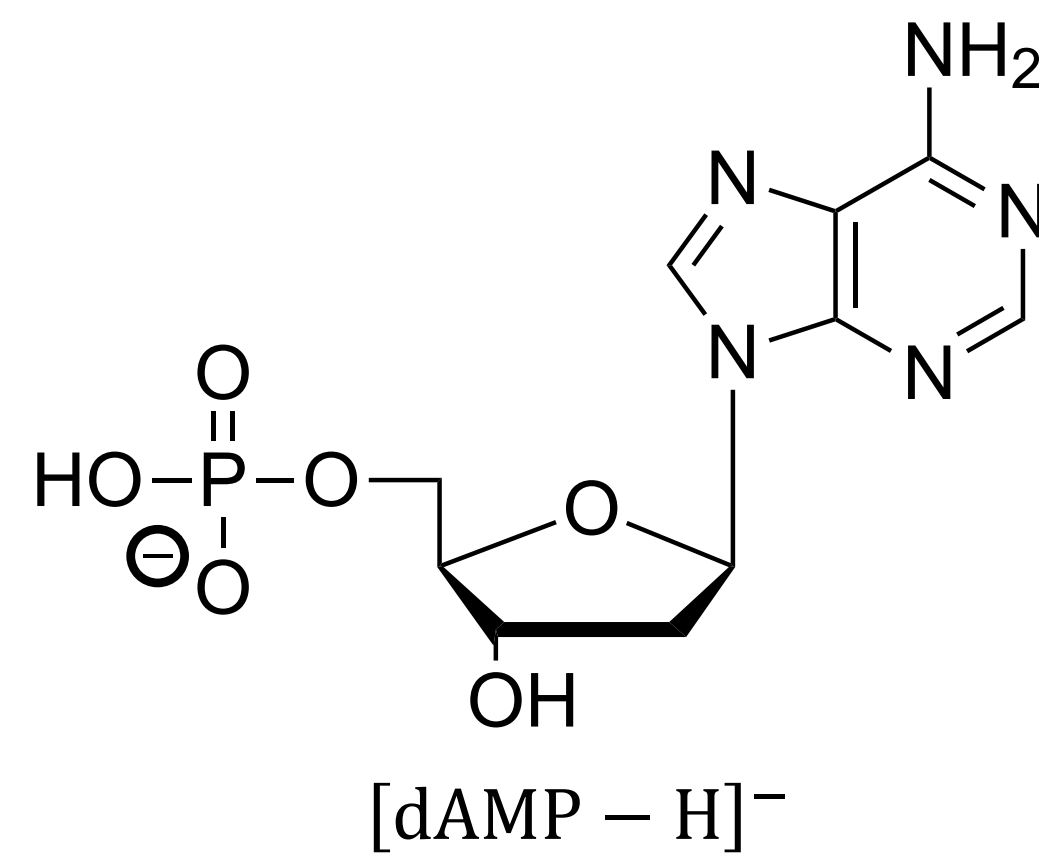
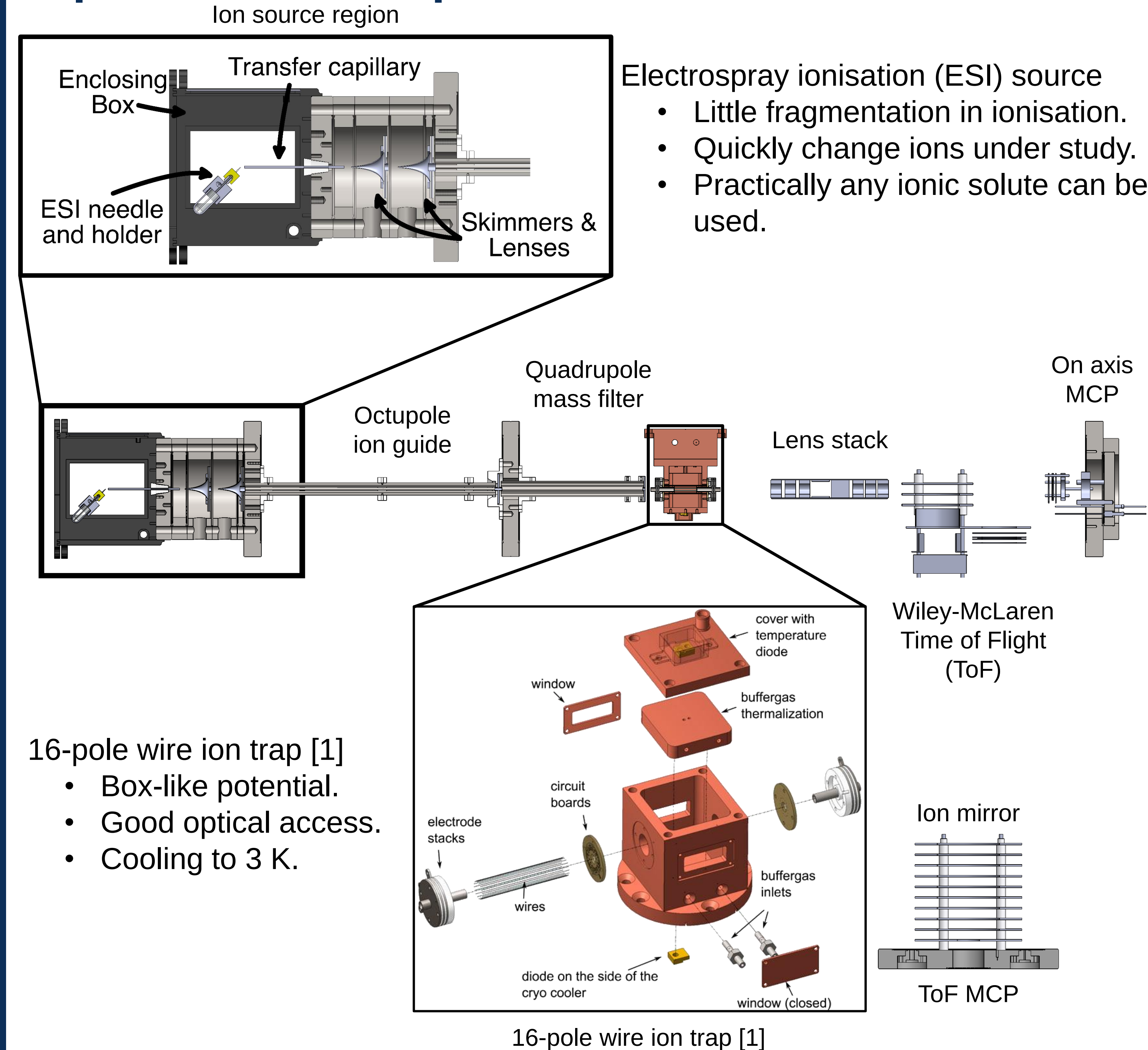


Motivation

- dAMP (2'-deoxyadenosine-5'-monophosphate) is a nucleotide in human DNA.
- dAMP fragments under UV-light:
 - Energy/wavelength dependence?
 - Fine structure?
 - Fragmentation behaviour?
 - Absolute cross section?



Experimental setup



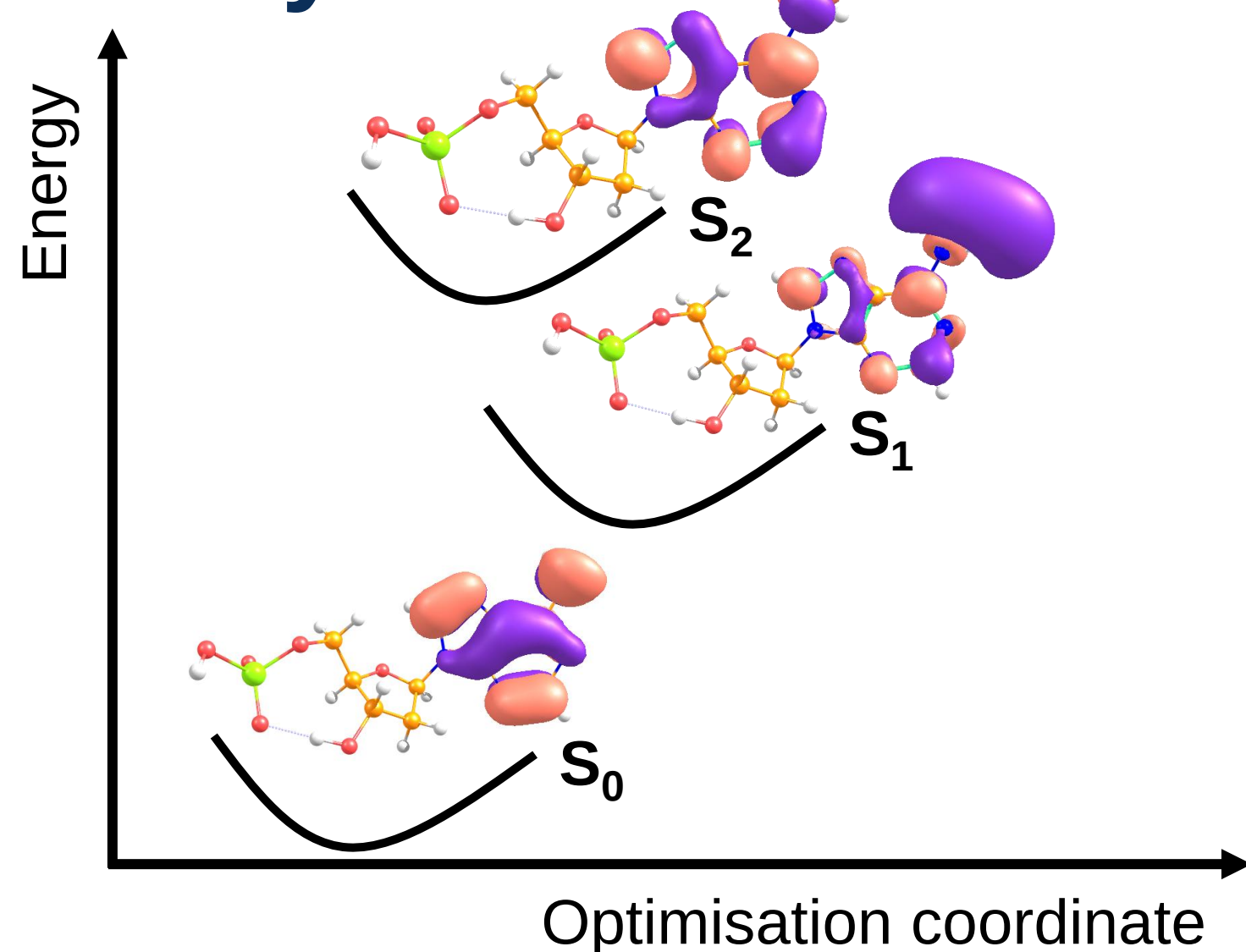
Electrospray ionisation (ESI) source

- Little fragmentation in ionisation.
- Quickly change ions under study.
- Practically any ionic solute can be used.

16-pole wire ion trap [1]

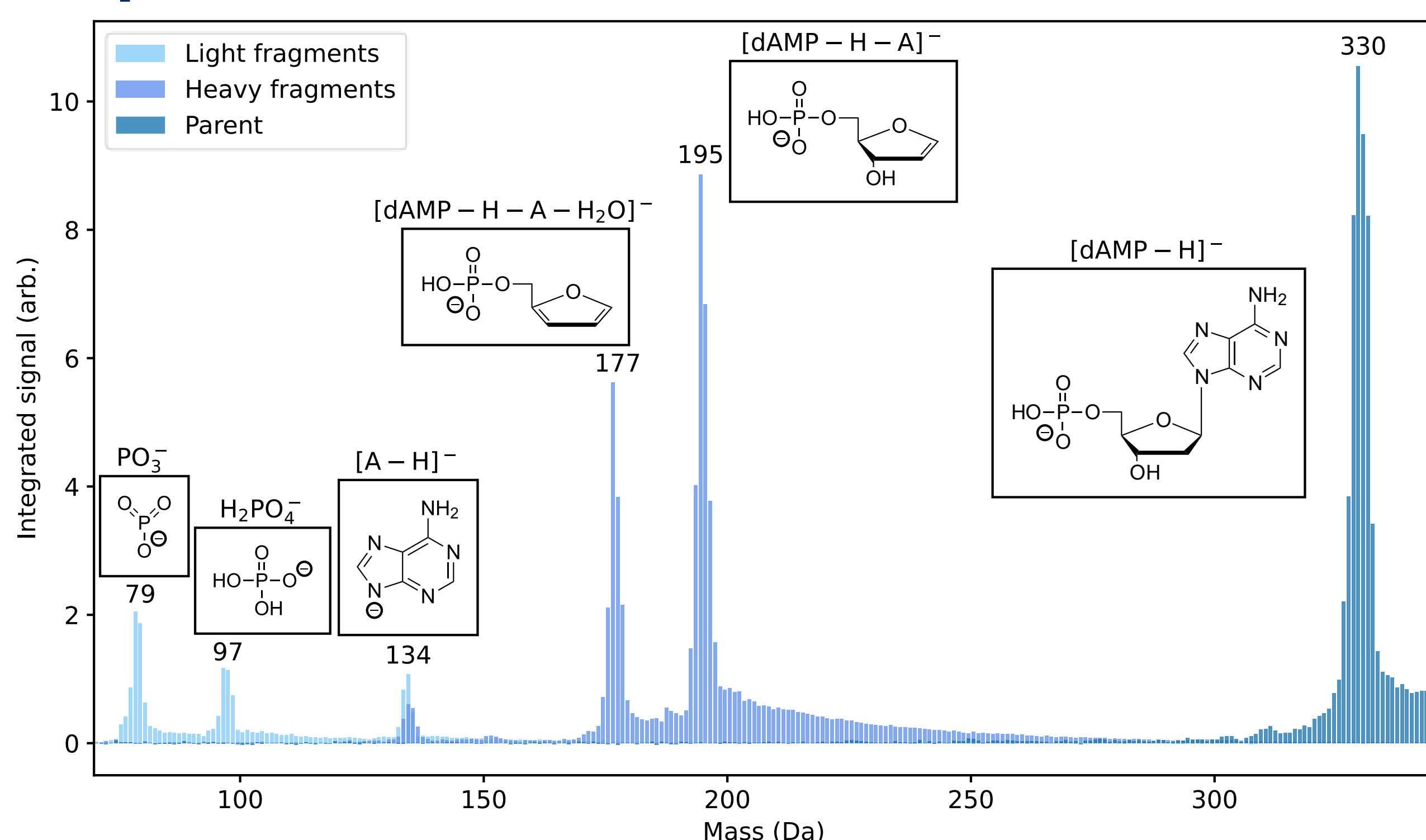
- Box-like potential.
- Good optical access.
- Cooling to 3 K.

Theory

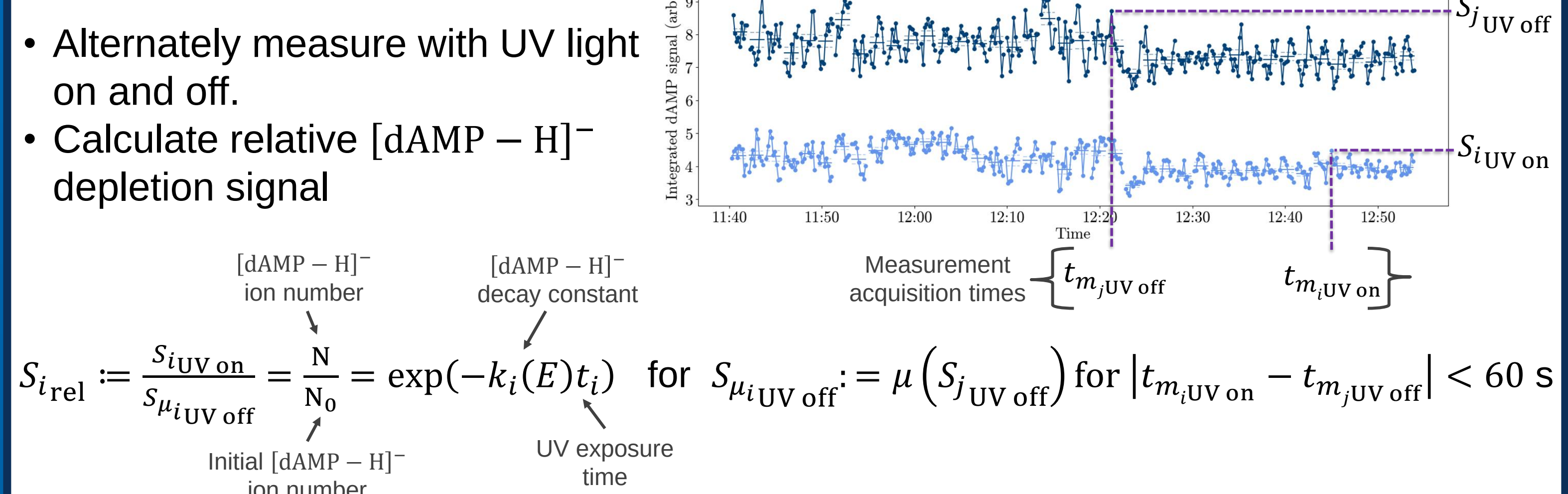


- Two accessible electronic excited states ($\pi \rightarrow \pi^*$ character).
- Many potential vibrational modes.
- Expect population of two energetically close ($\Delta E = 0.01$ eV) isomers.

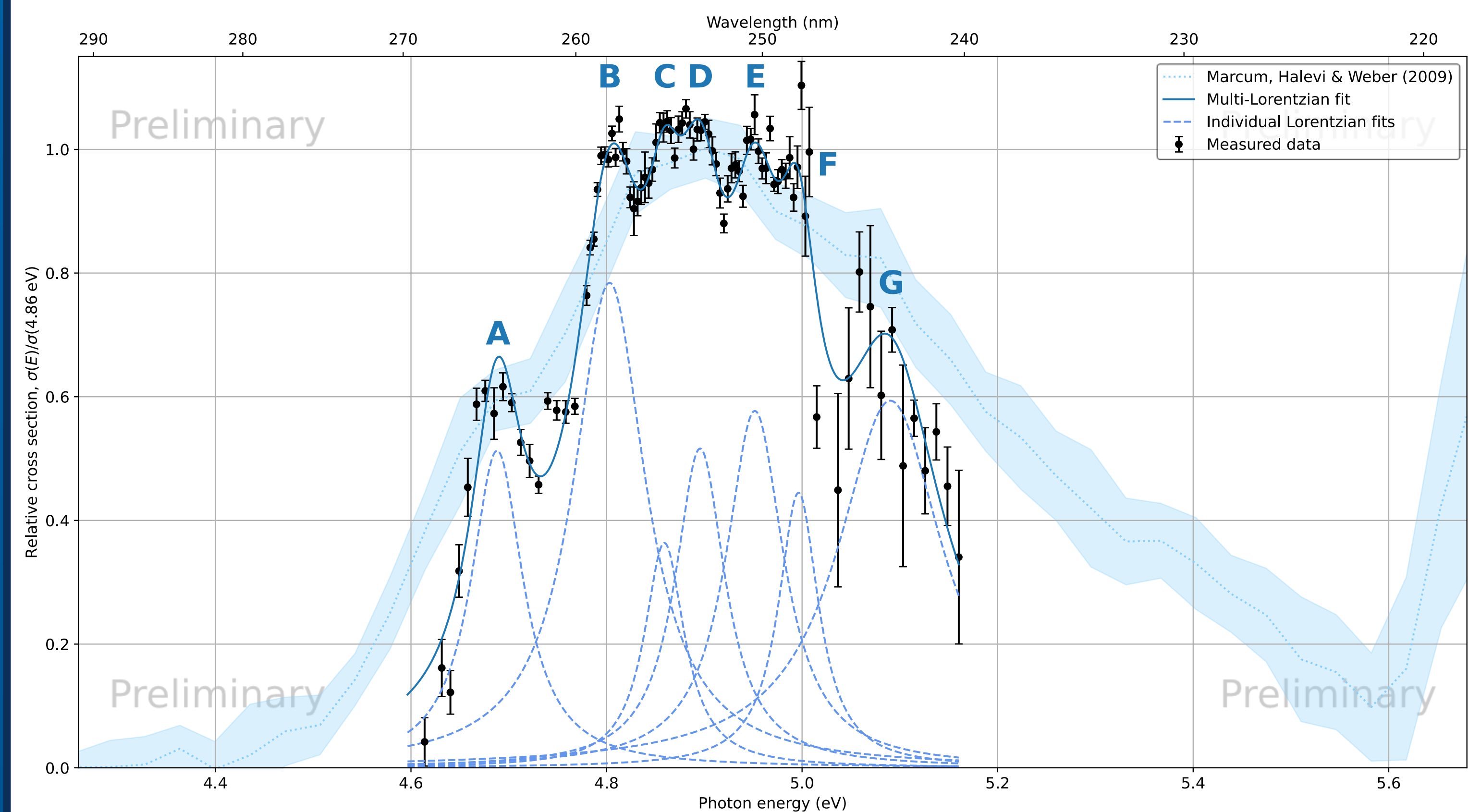
Mass spectrum



Spectrum

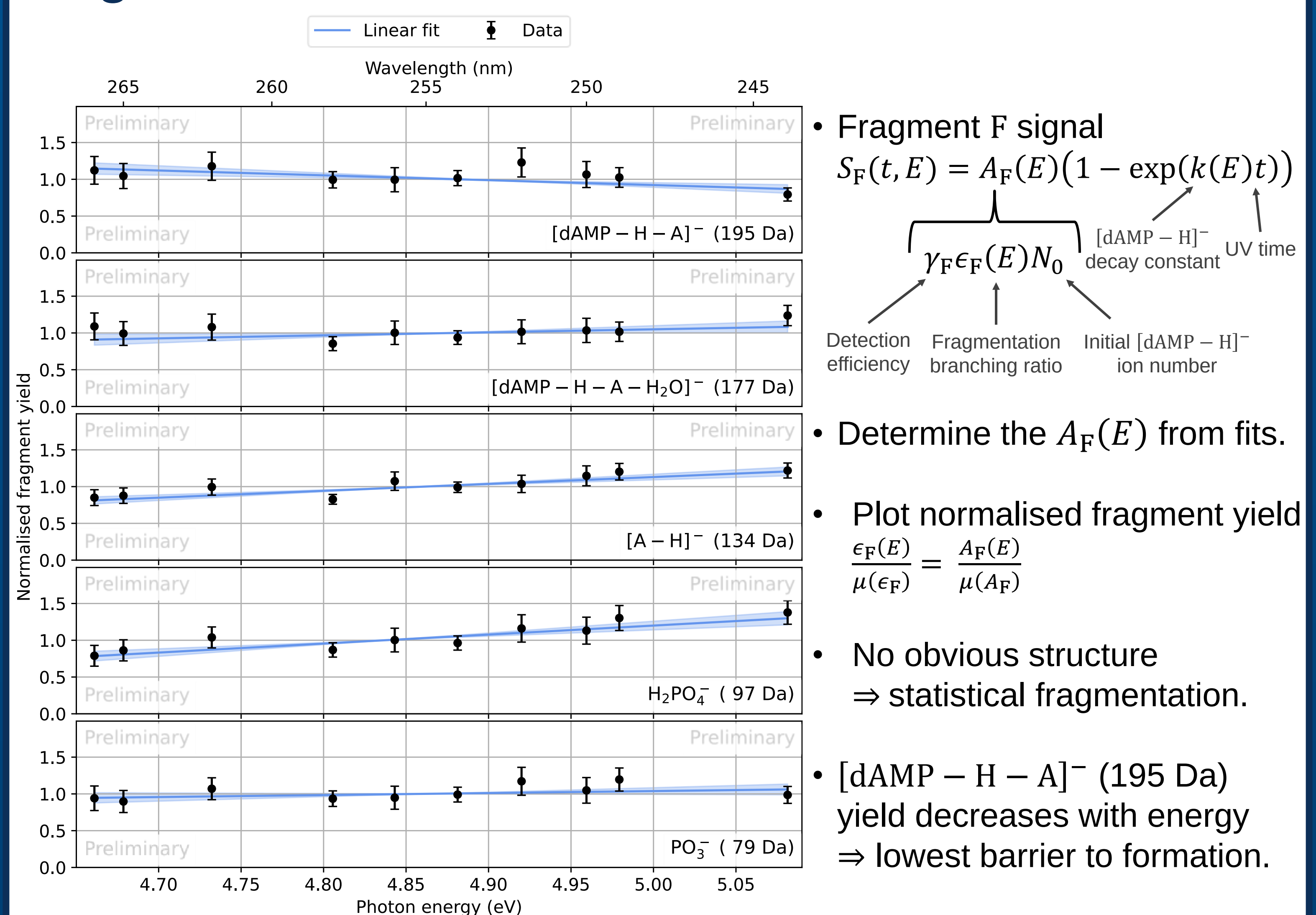


- Normalise against laser power and daily reference measurement.
- Compensate for slow drifts during day (empirical scaling factor).



- Obtain cross section relative to 4.86 eV (255 nm).
- Good agreement to literature [2] with additional fine structure found.
- Absolute value $\sigma_{[dAMP-H]^-}(4.86 \text{ eV}) \approx 2\sigma_{I^-}(4.86 \text{ eV})$.

Fragmentation



Fragment F signal

$$S_F(t, E) = A_F(E)(1 - \exp(k(E)t))$$

Parameters: $\gamma_F \epsilon_F(E) N_0$ (Detection efficiency), $\epsilon_F(E)$ (Fragmentation branching ratio), N_0 (Initial [dAMP - H]⁻ ion number), $k(E)$ (decay constant), t (UV time).

- Determine the $A_F(E)$ from fits.
- Plot normalised fragment yield $\frac{\epsilon_F(E)}{\mu(\epsilon_F)} = \frac{A_F(E)}{\mu(A_F)}$
- No obvious structure $\Rightarrow$ statistical fragmentation.
- [dAMP - H - A]⁻ (195 Da) yield decreases with energy $\Rightarrow$ lowest barrier to formation.

Outlook

- More precise value for absolute dAMP cross section.
- Further scans at higher photon energy.
- Comparison to other nucleotides e.g. dCMP.

