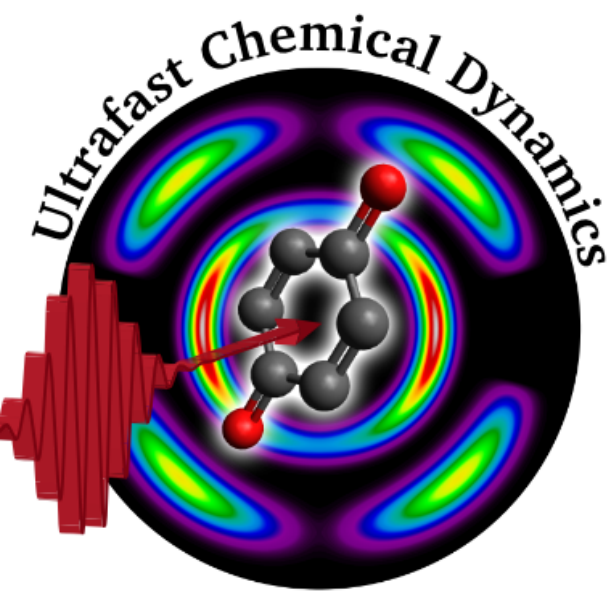


Mapping complex photochemical reactions using femtosecond UV-pump XUV-probe photoelectron spectroscopy

Dr. Daniel A. Horke

Ultrafast Chemical Dynamics group

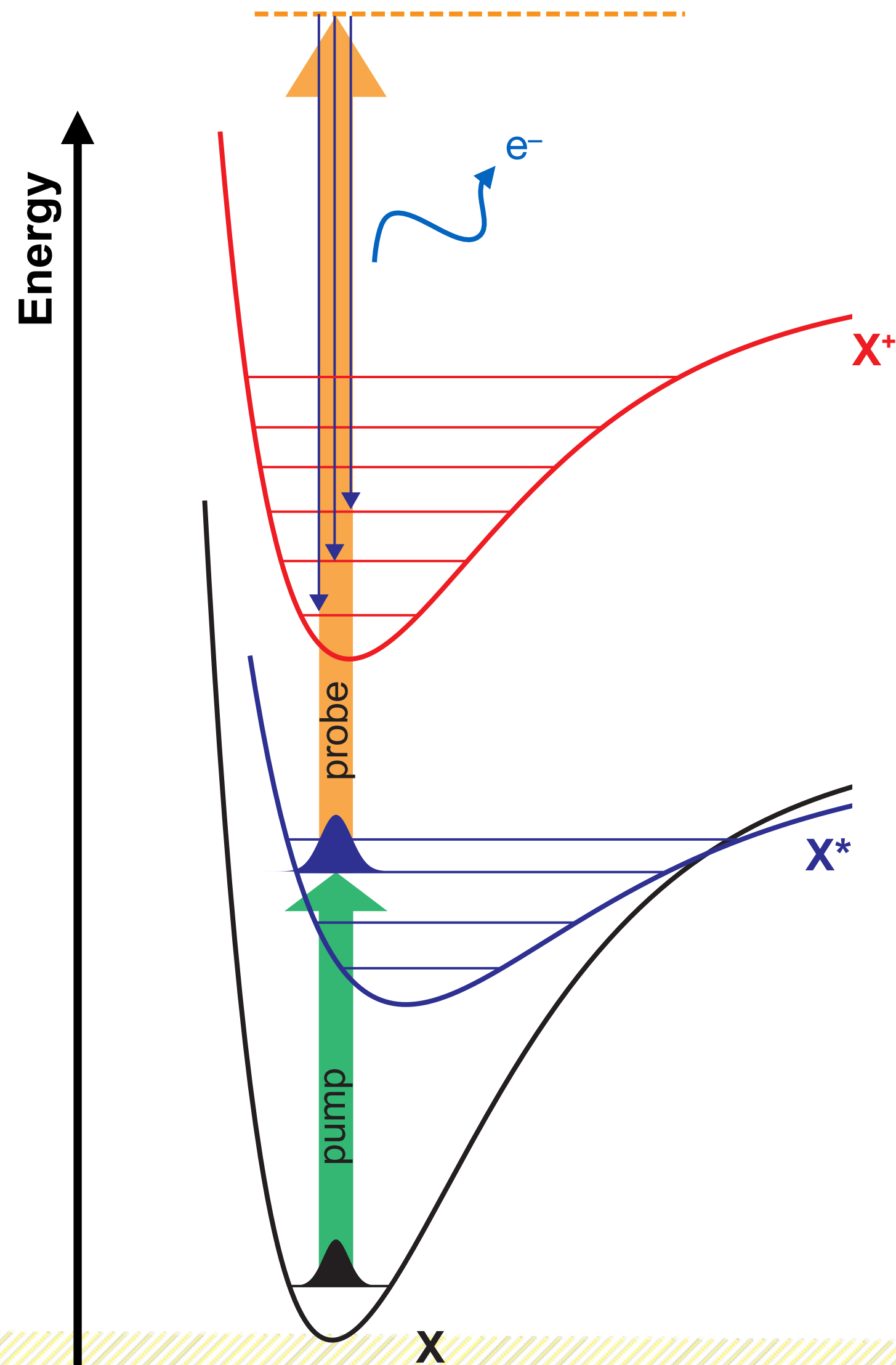
Spectroscopy of Cold Molecules Dept., Institute for Molecules & Materials, Radboud University, Nijmegen



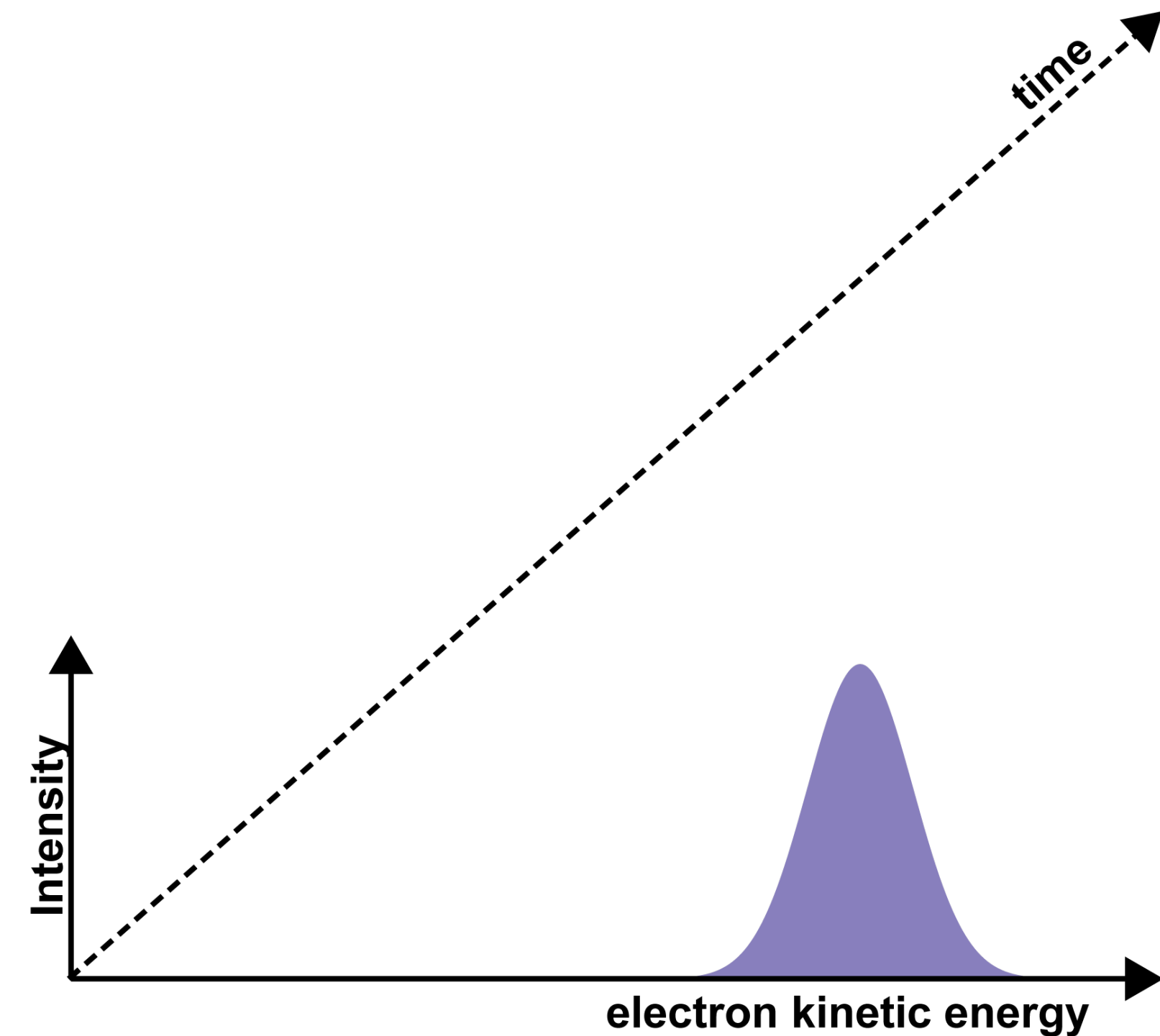
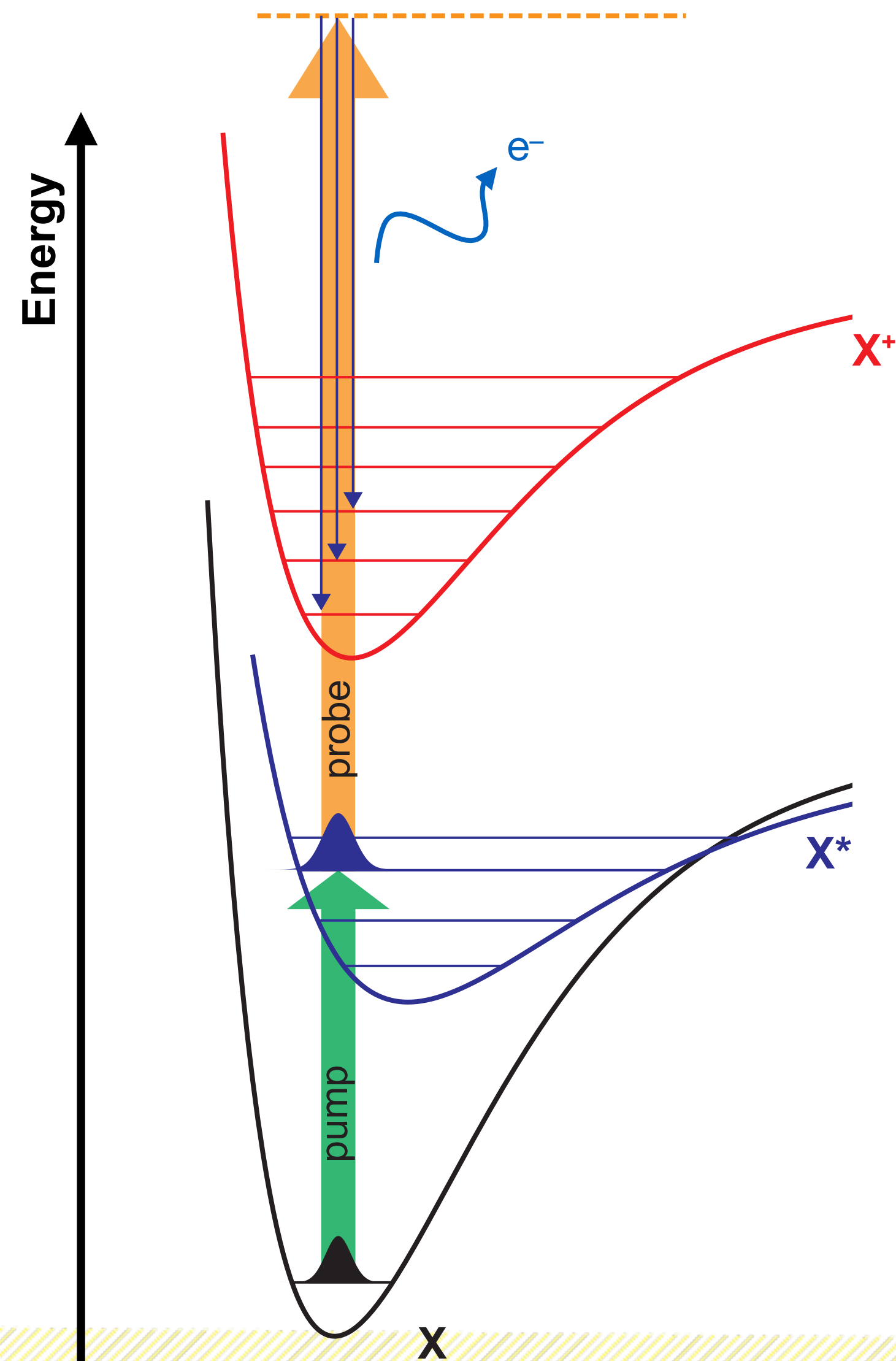
Radboud University



Time-resolved photoelectron spectroscopy – a direct probe for electronic state populations –

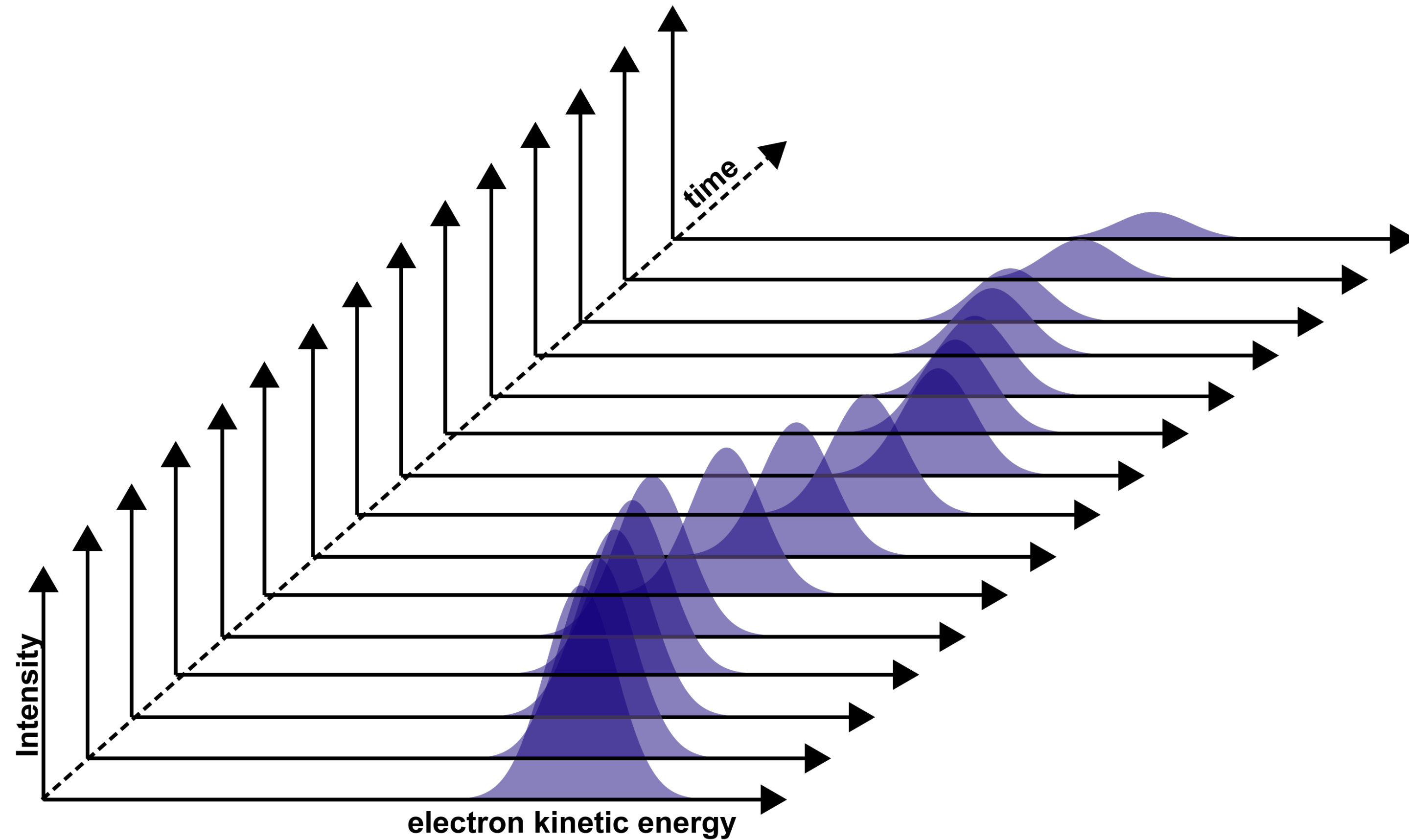
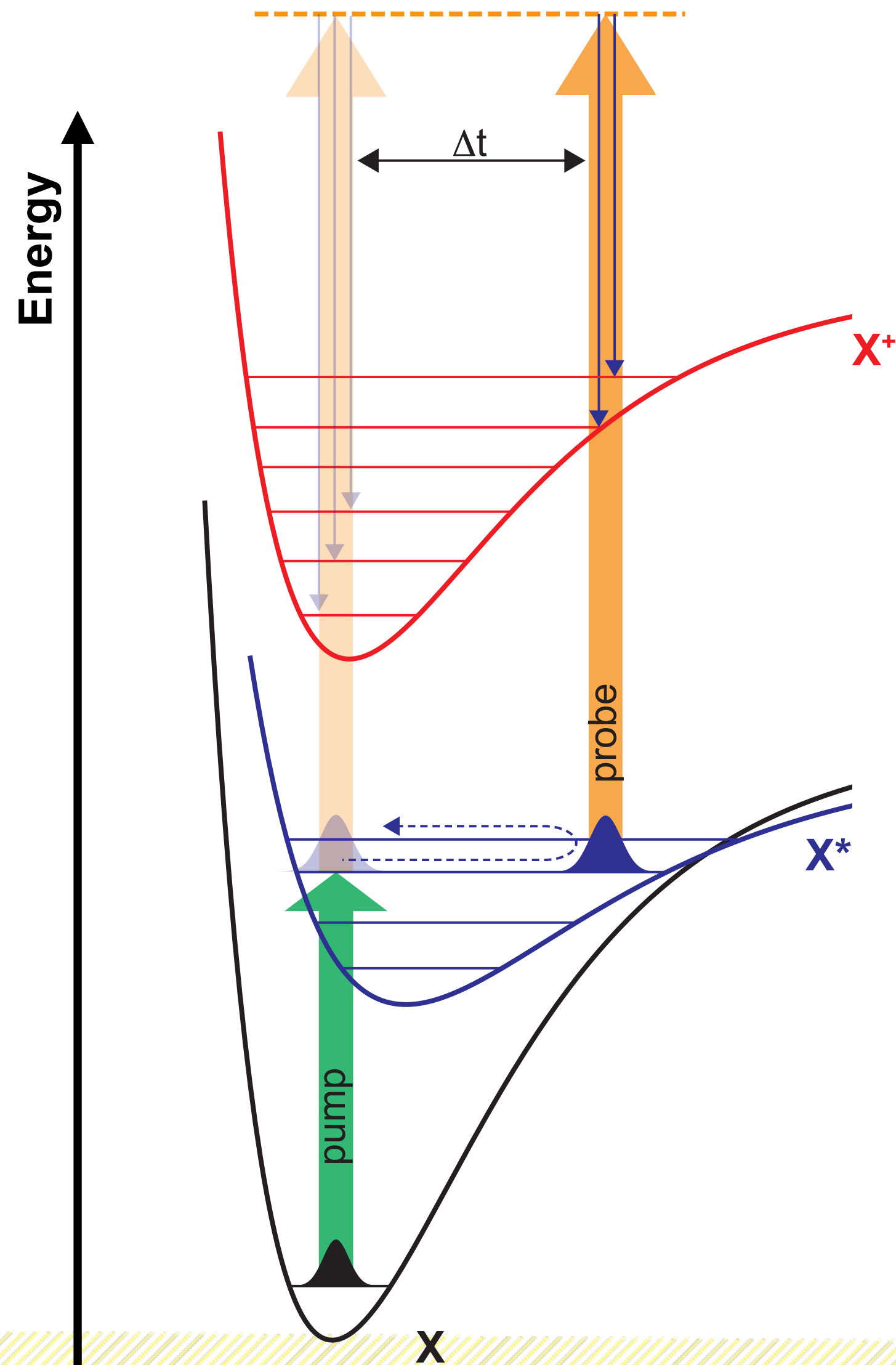


Time-resolved photoelectron spectroscopy – a direct probe for electronic state populations –



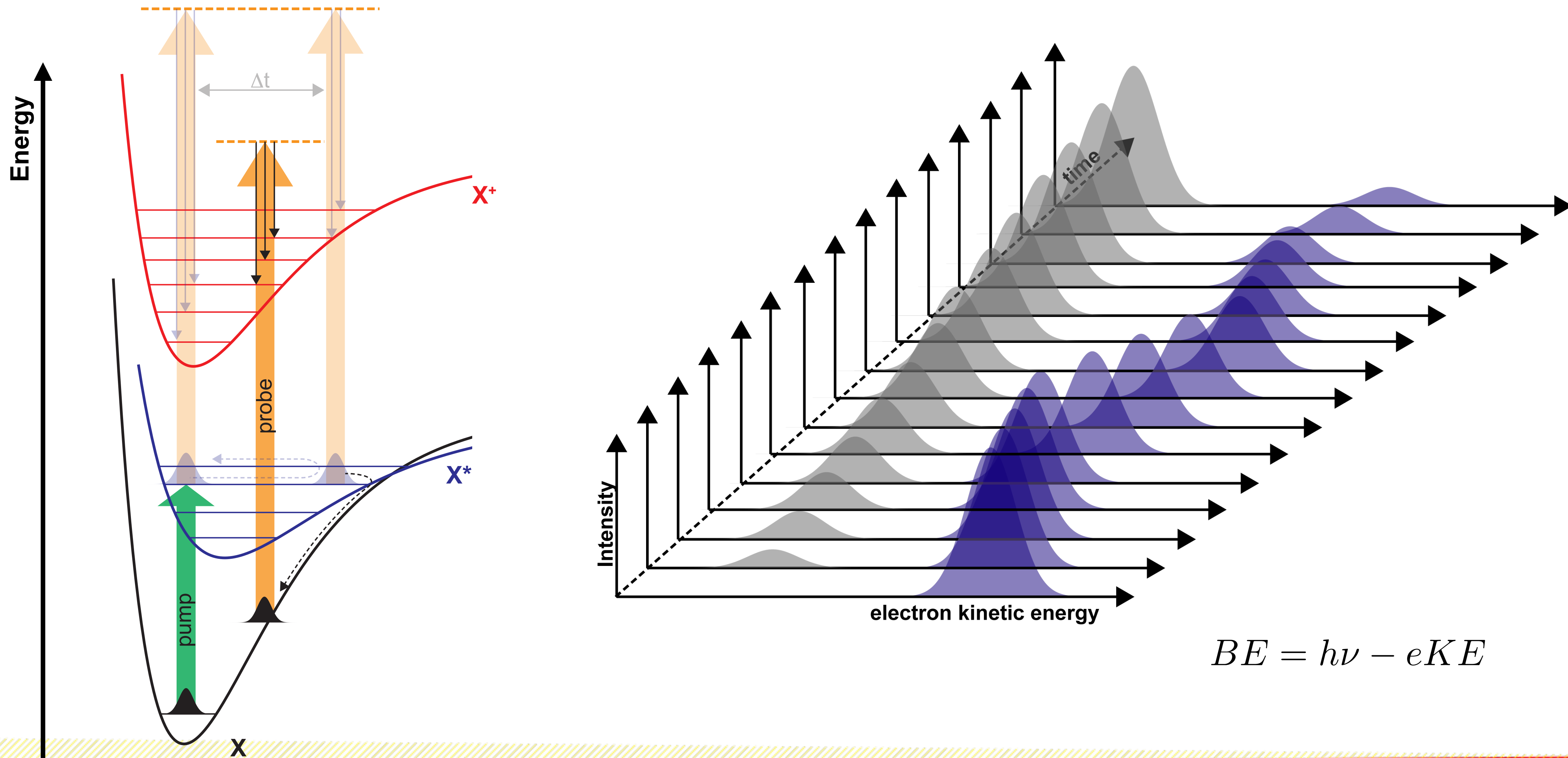
$$BE = h\nu - eKE$$

Time-resolved photoelectron spectroscopy – a direct probe for electronic state populations –



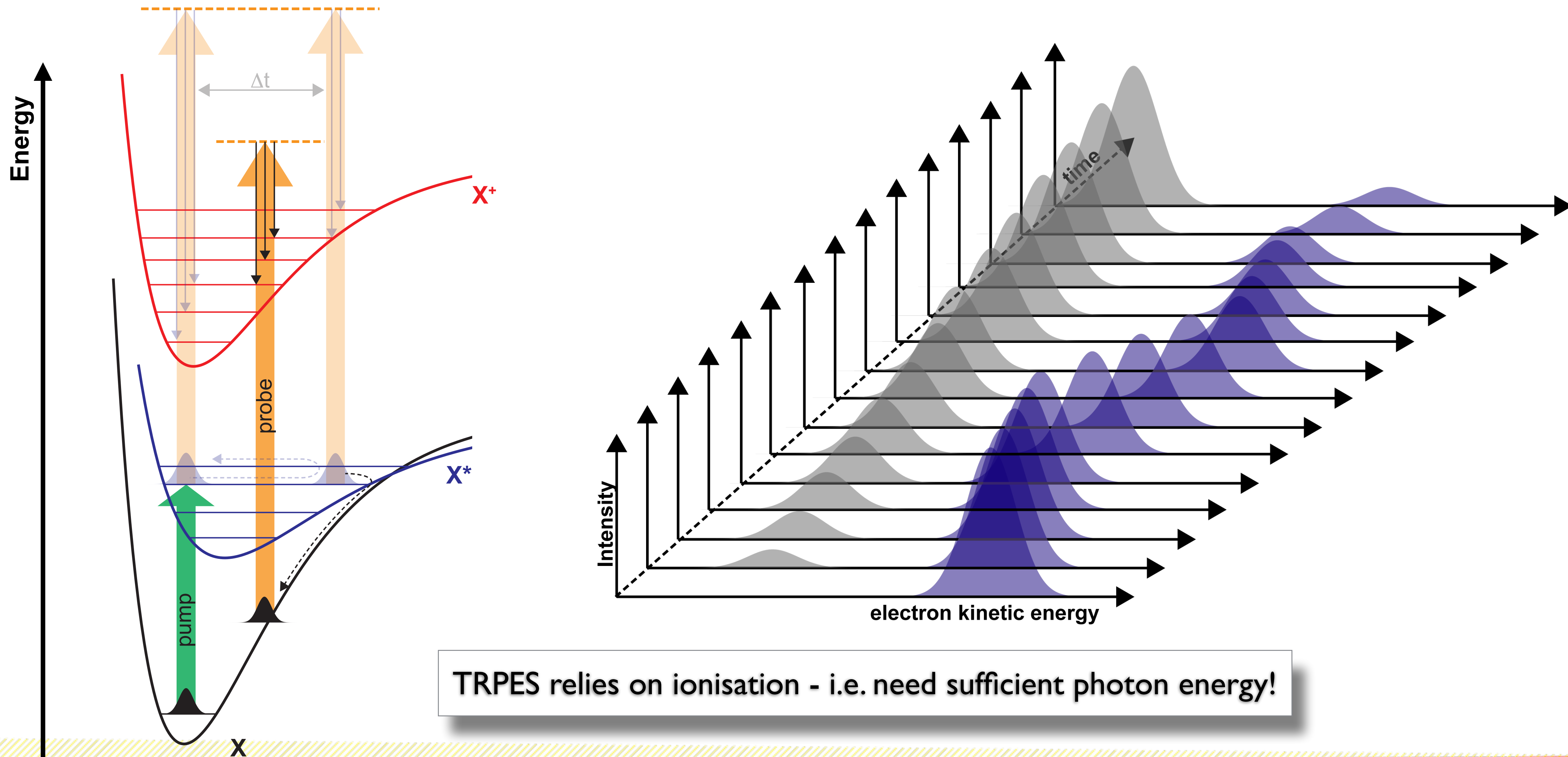
$$BE = h\nu - eKE$$

Time-resolved photoelectron spectroscopy – a direct probe for electronic state populations –



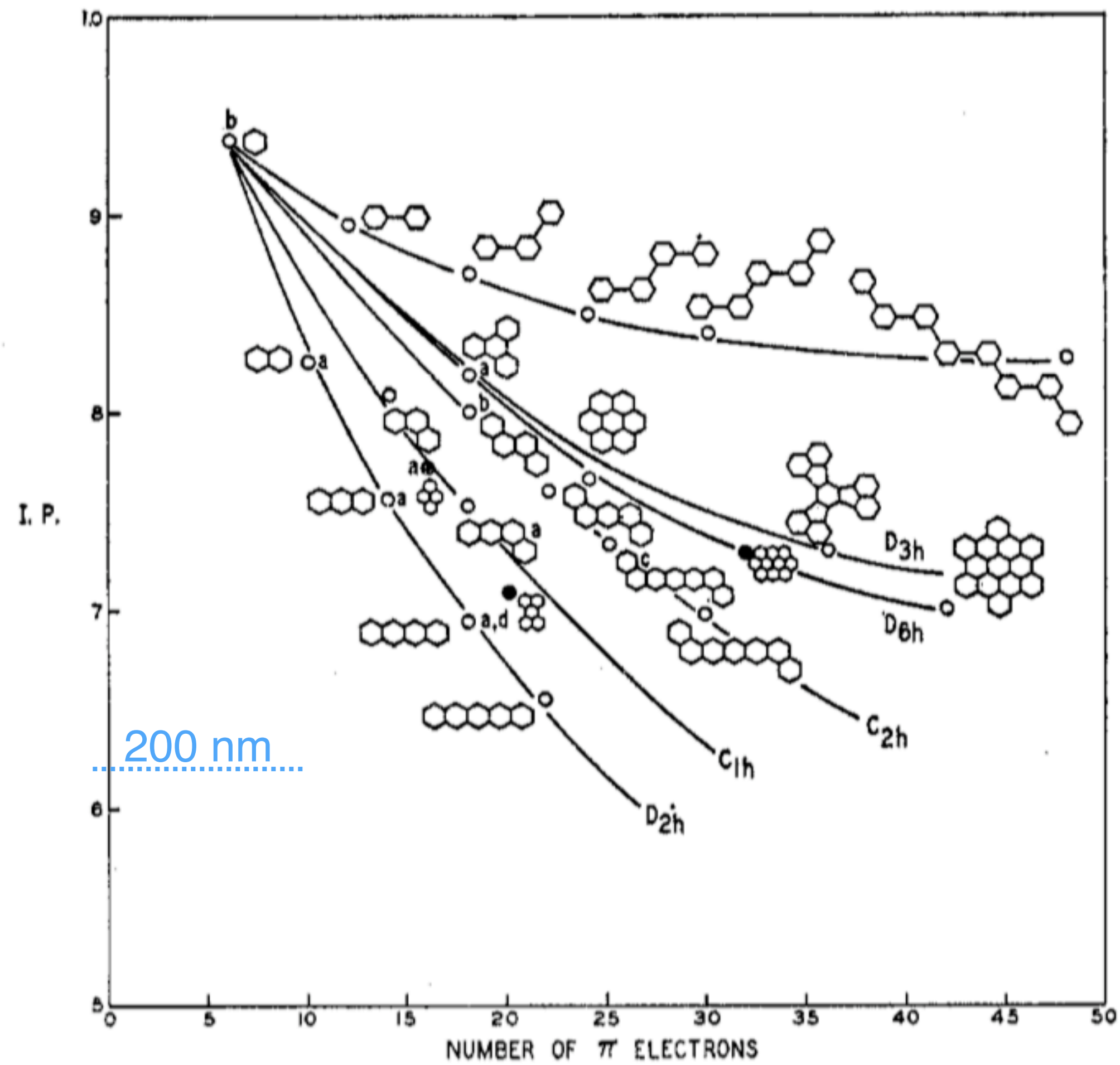
$$BE = h\nu - eKE$$

Time-resolved photoelectron spectroscopy – a direct probe for electronic state populations –



TRPES relies on ionisation - i.e. need sufficient photon energy!

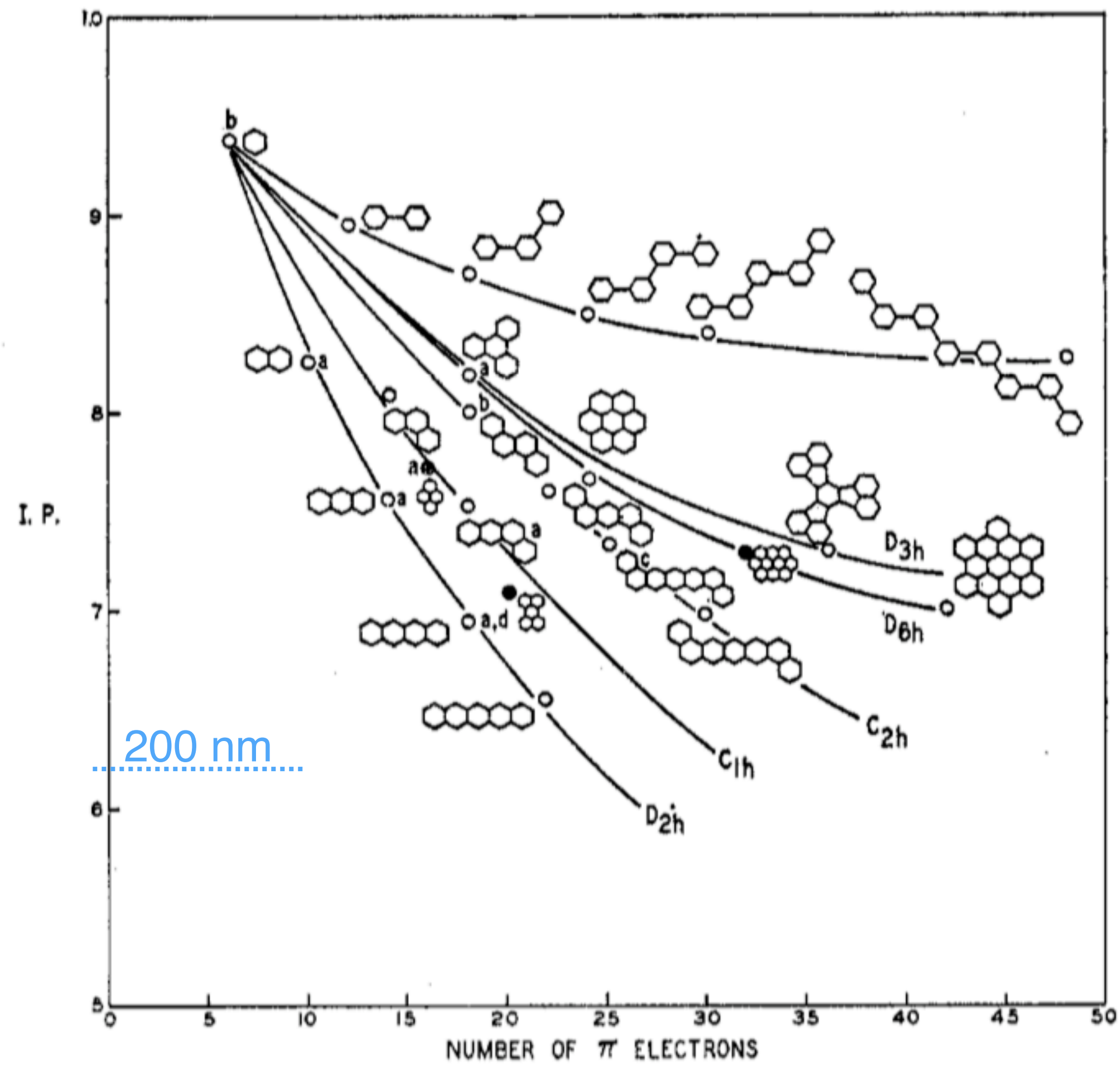
Available photon energy restricts the observation window



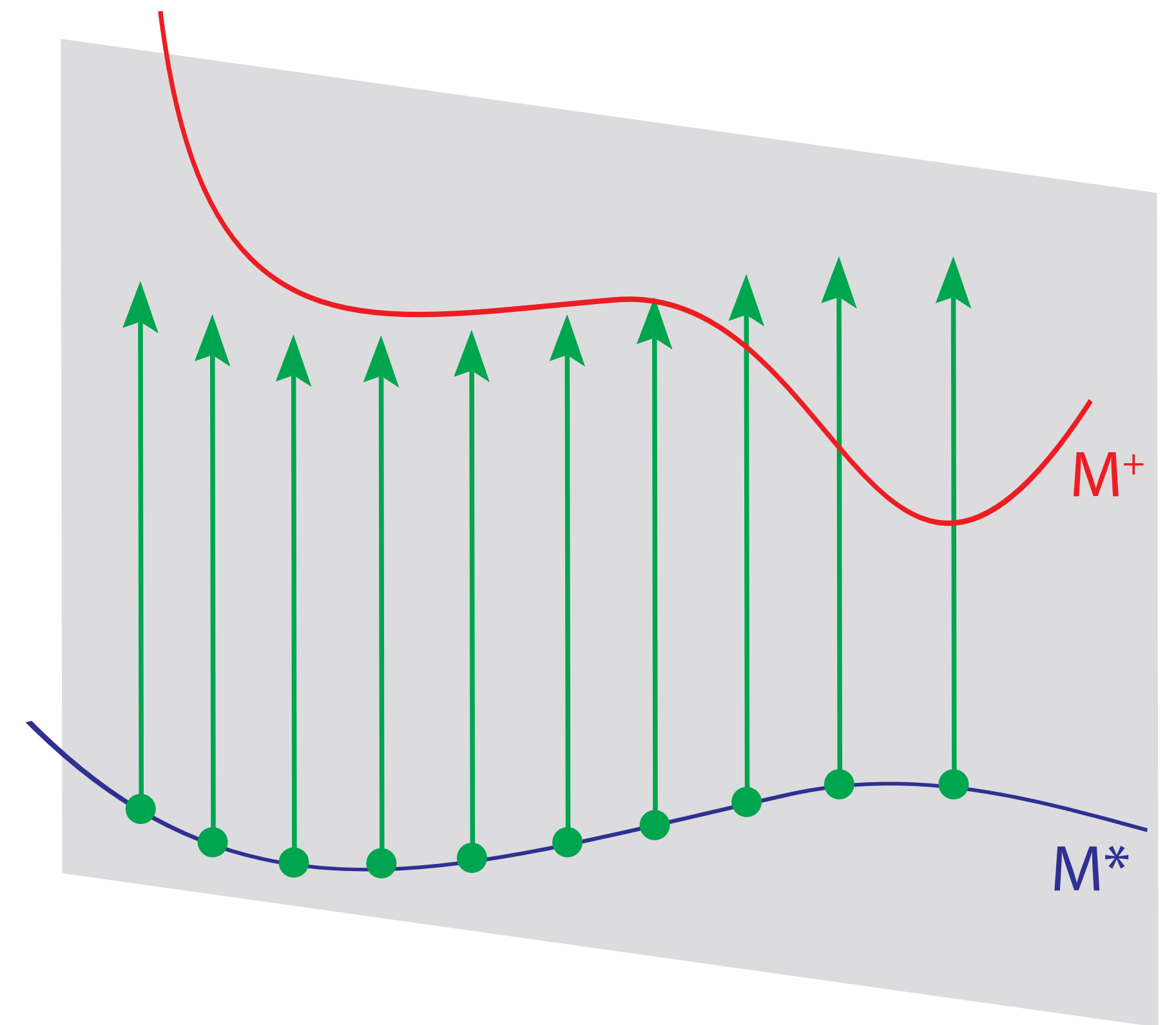
Gallegos, J. Phys. Chem. 72, 3452 (1968)



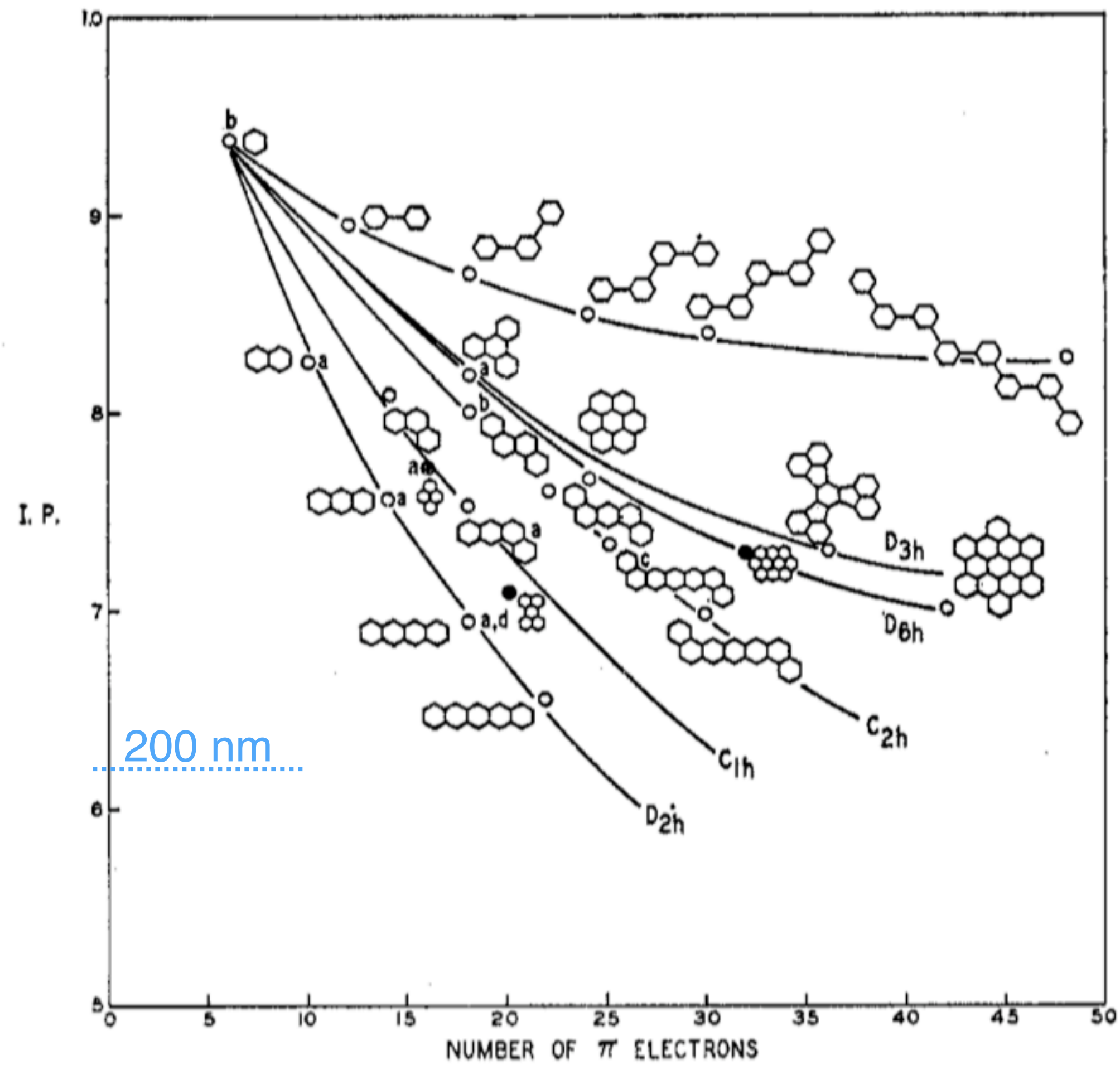
Available photon energy restricts the observation window



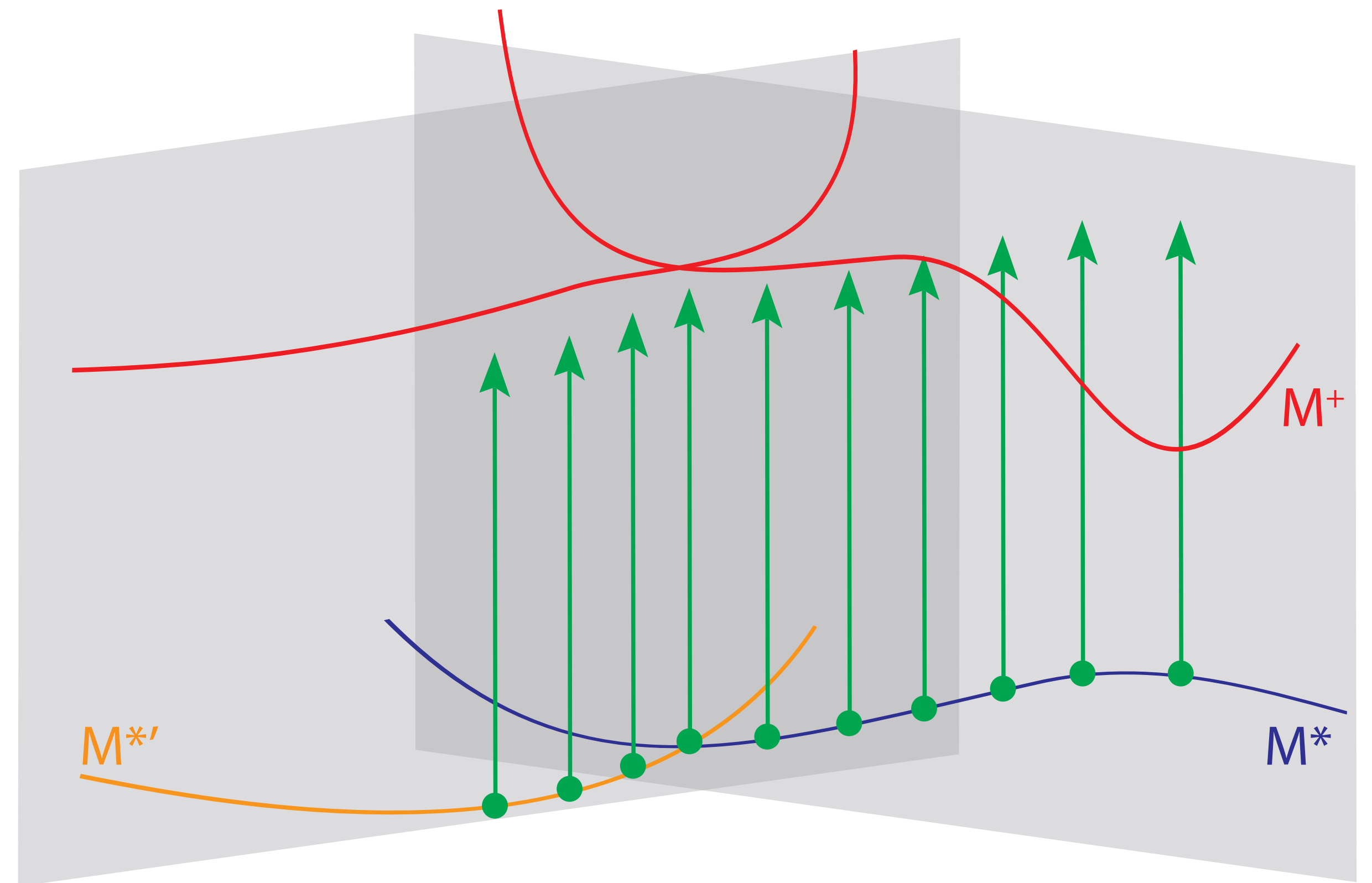
Gallegos, J. Phys. Chem. 72, 3452 (1968)



Available photon energy restricts the observation window



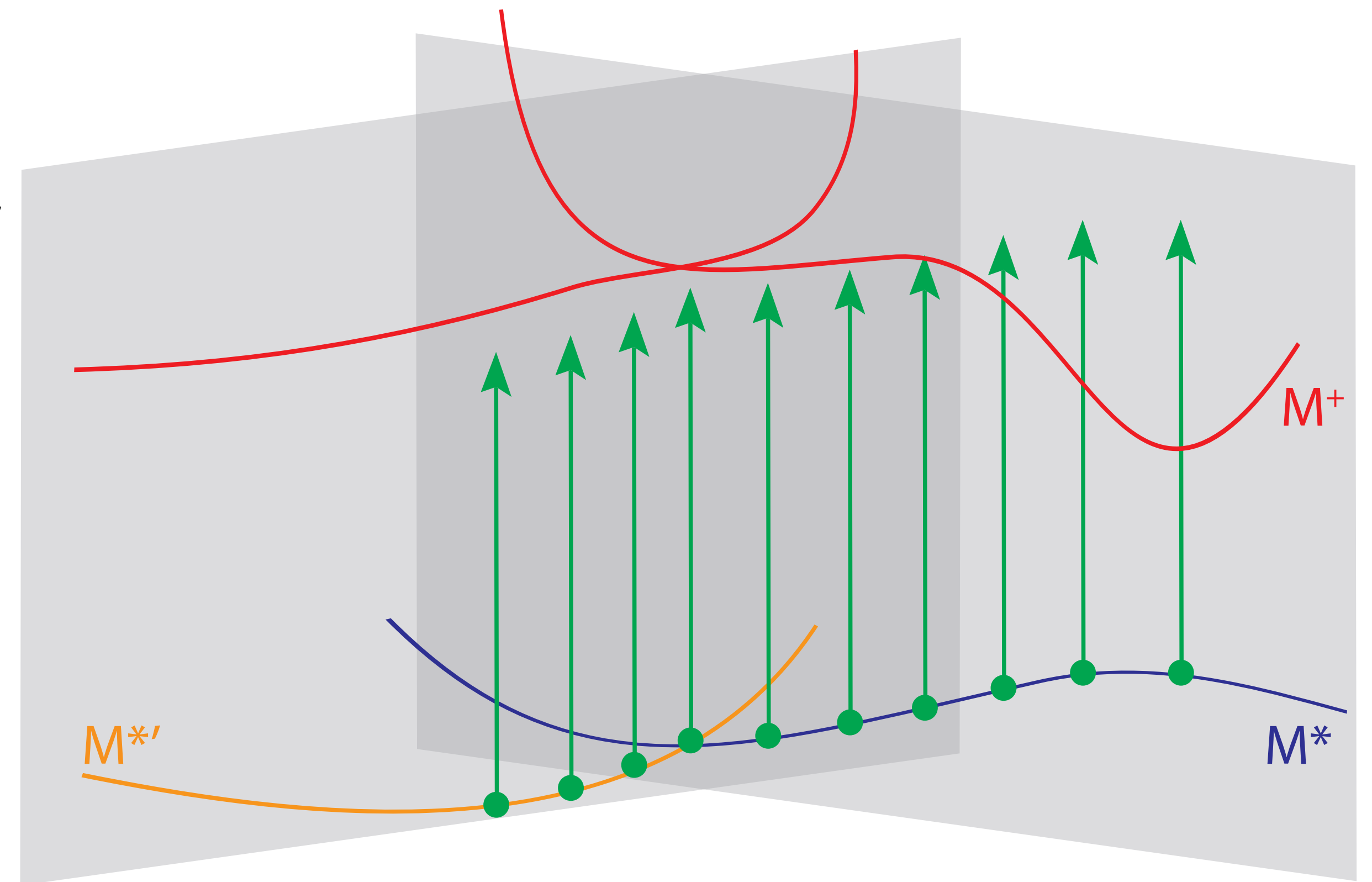
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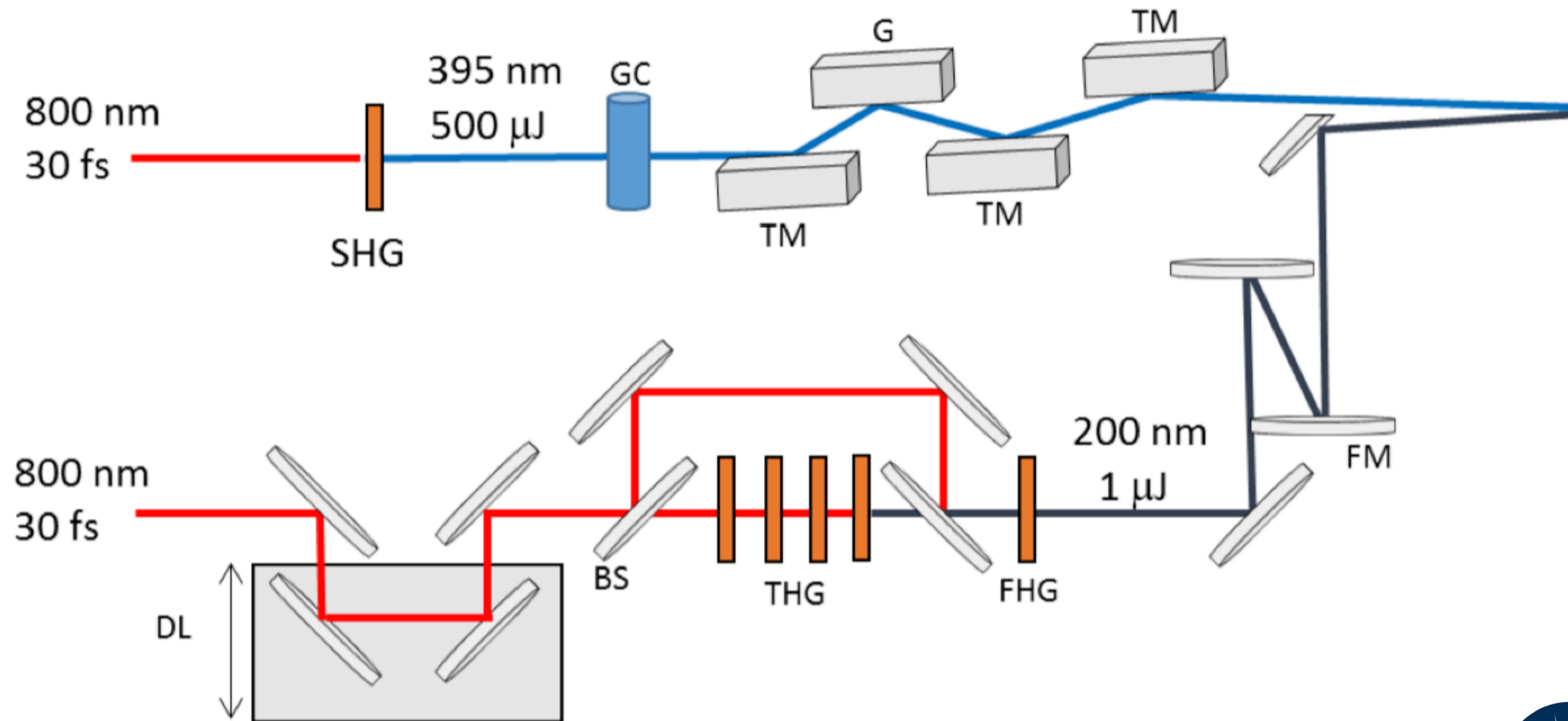
Dynamics in neutrals - restricted observation window – *why we need XUV lasers* –

- Available probe energy restricts the observation window
- We are then essentially 'blind' - cannot distinguish population transfer from nuclear dynamics
- Nuclear dynamics (mostly) rules out REMPI schemes

↳ **Ultrashort XUV pulses!**



UV-pump XUV-probe photoelectron spectroscopy



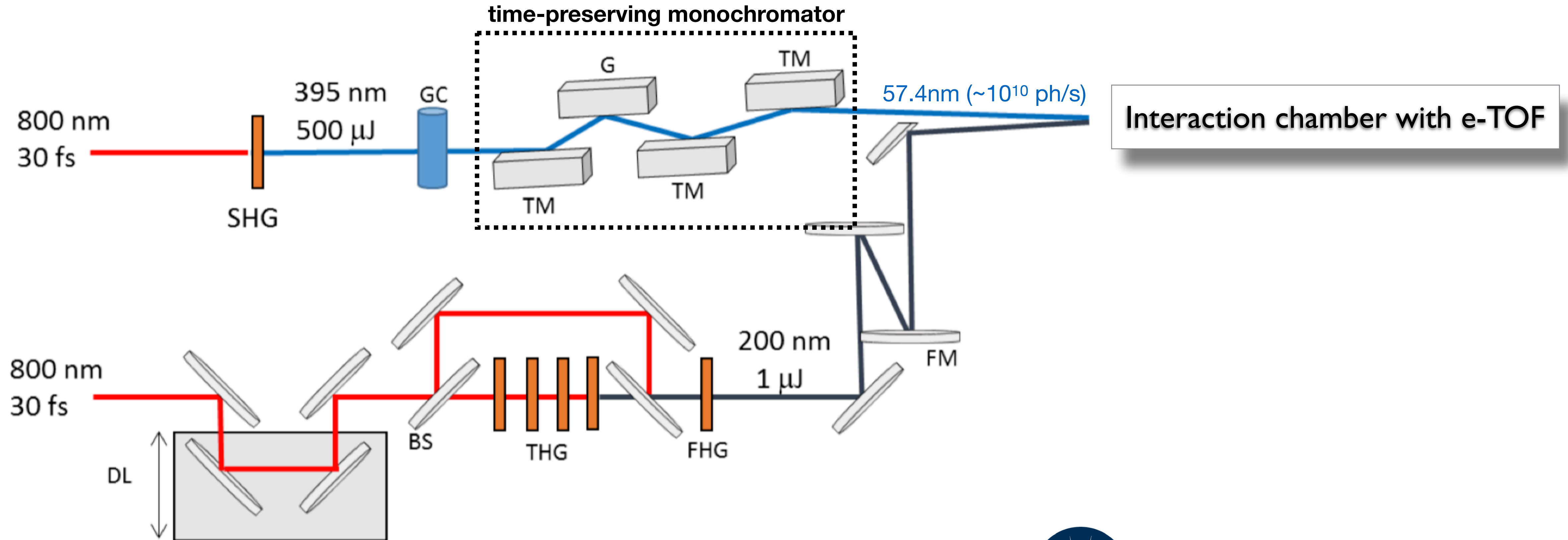
Frasetto et al, *Opt. Expr.* **19**, 19169 (2011)



Science & Technology Facilities Council
Rutherford Appleton Laboratory
Artemis facility (Emma Springate)

Russell Minns (U Southampton)
Adam Kirrander (U Edinburgh)

UV-pump XUV-probe photoelectron spectroscopy



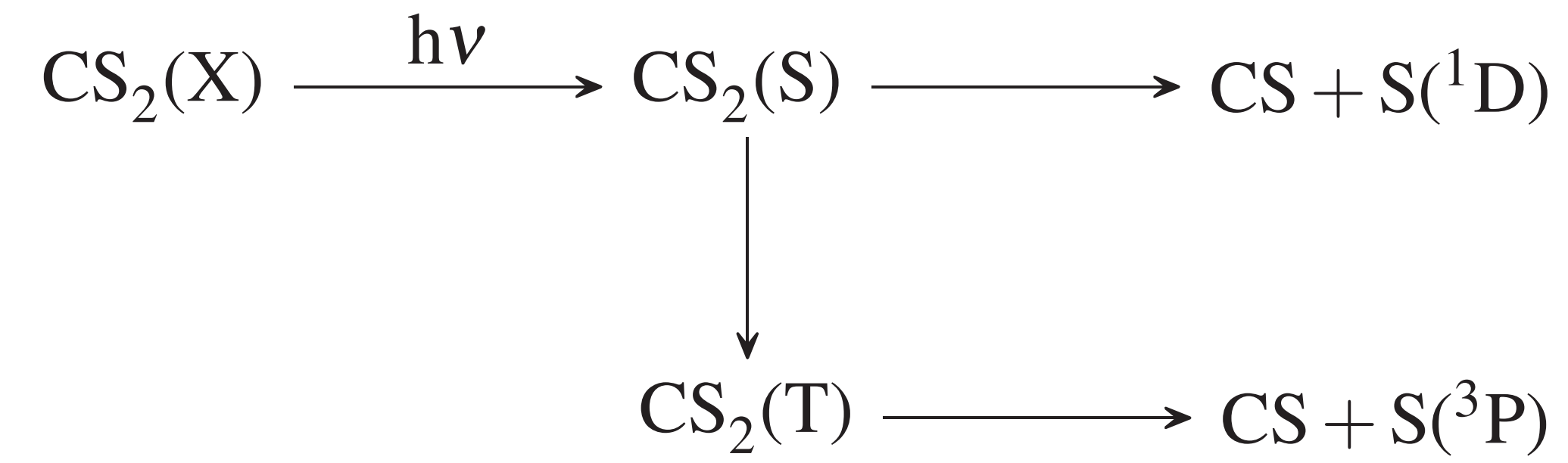
Frasetto et al, *Opt. Expr.* **19**, 19169 (2011)



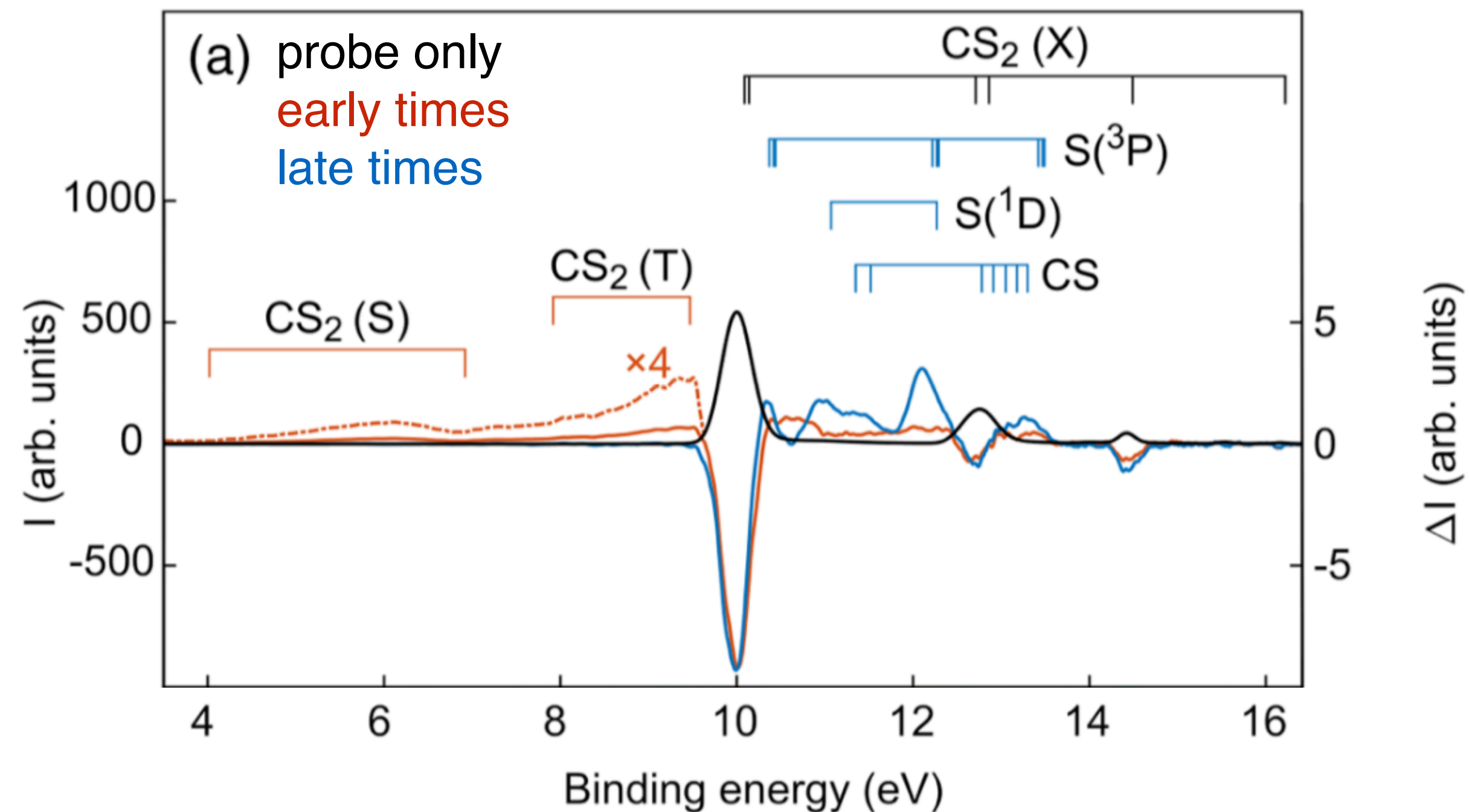
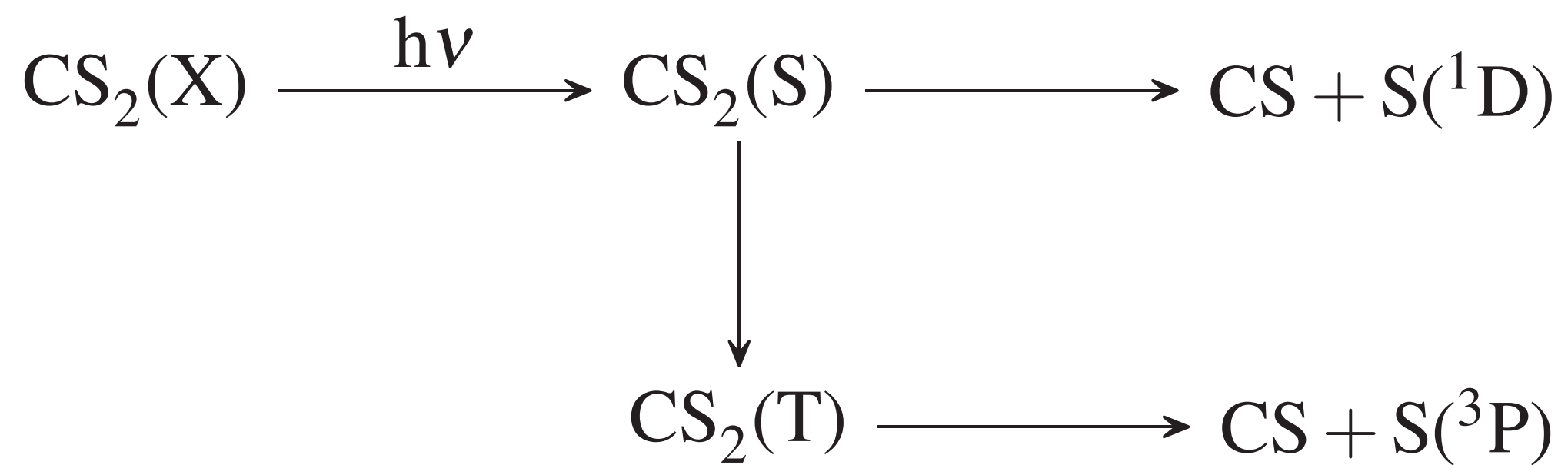
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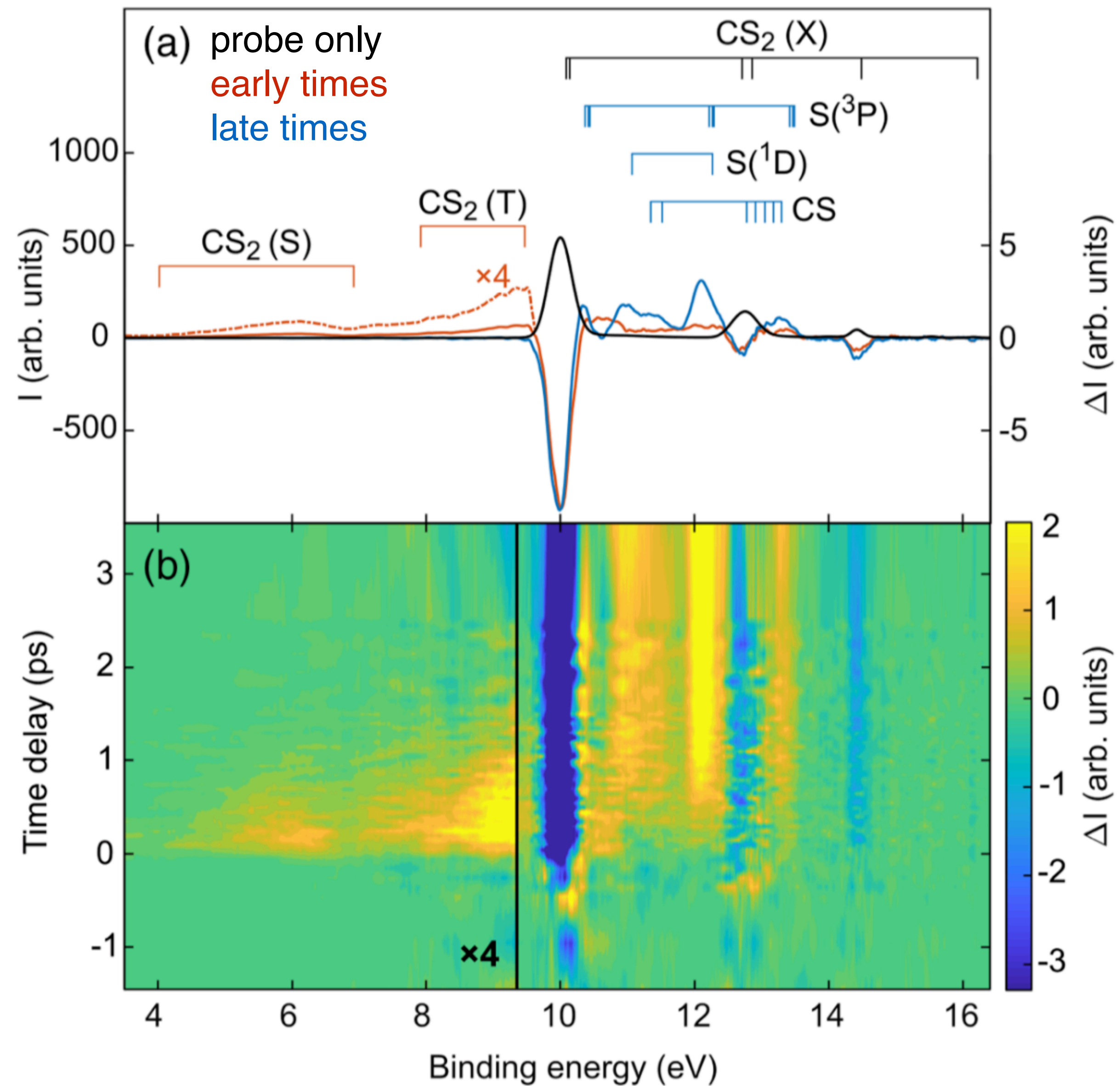
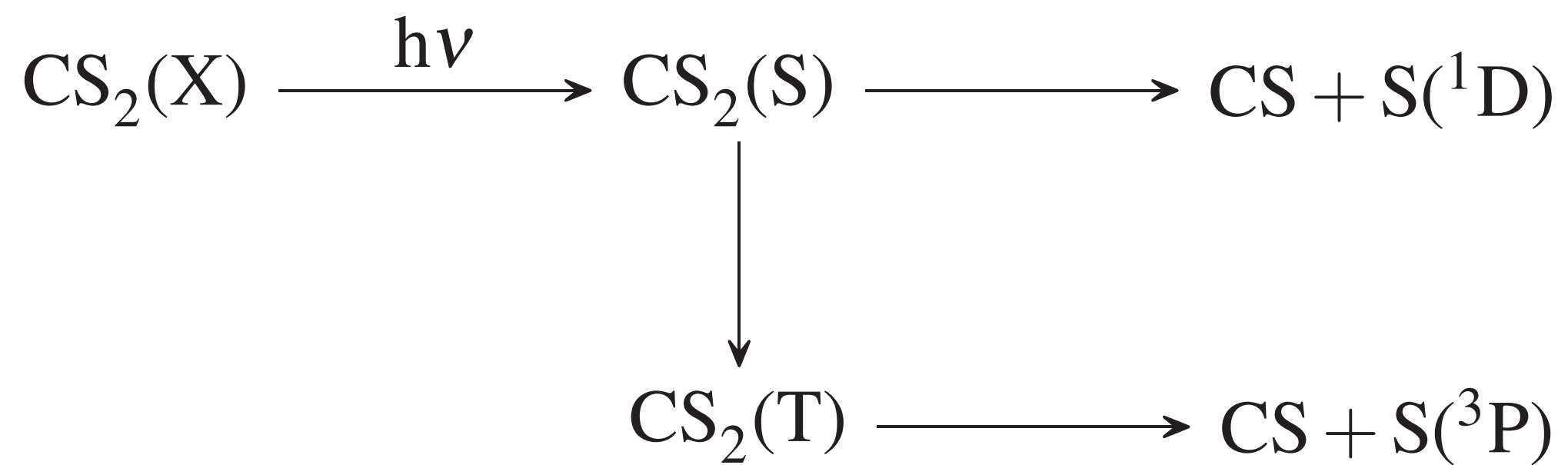
Mapping a complete photochemical reaction



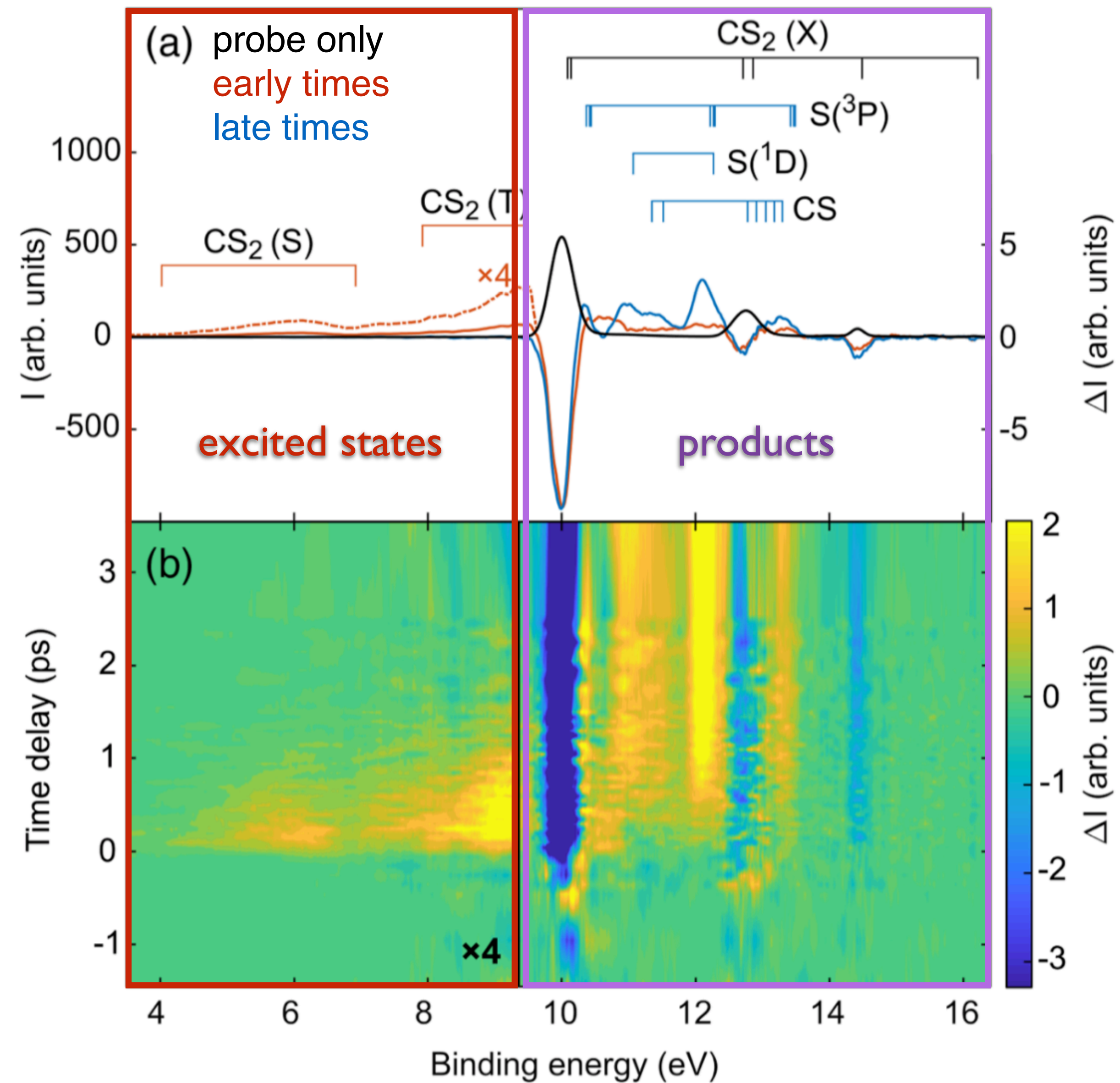
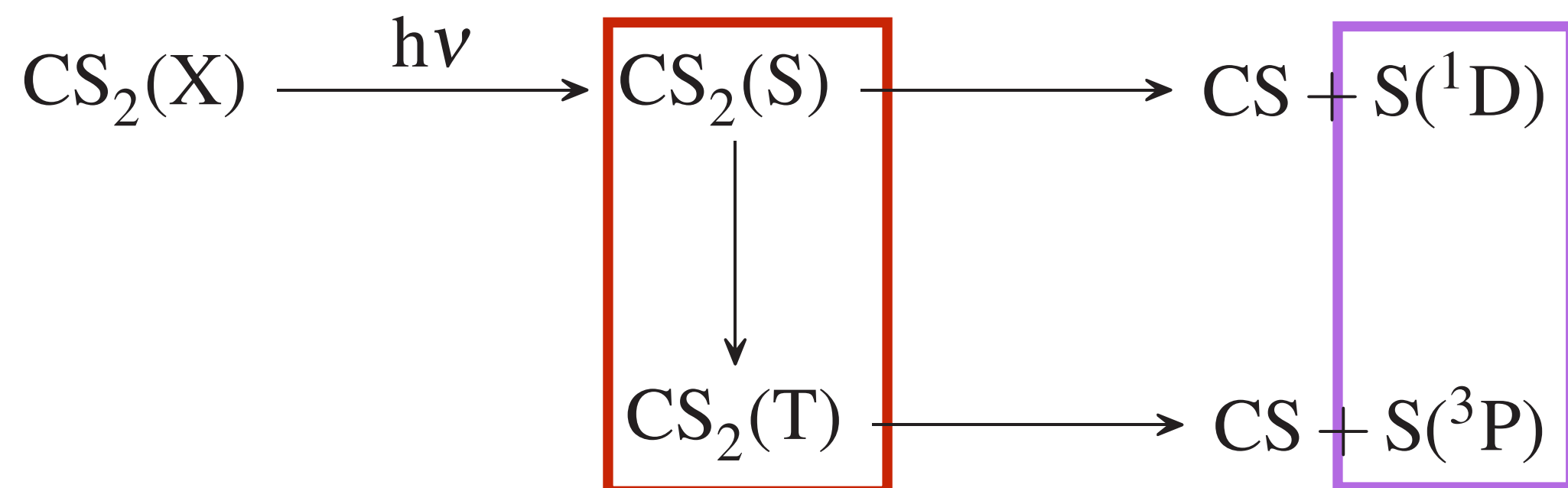
Mapping a complete photochemical reaction



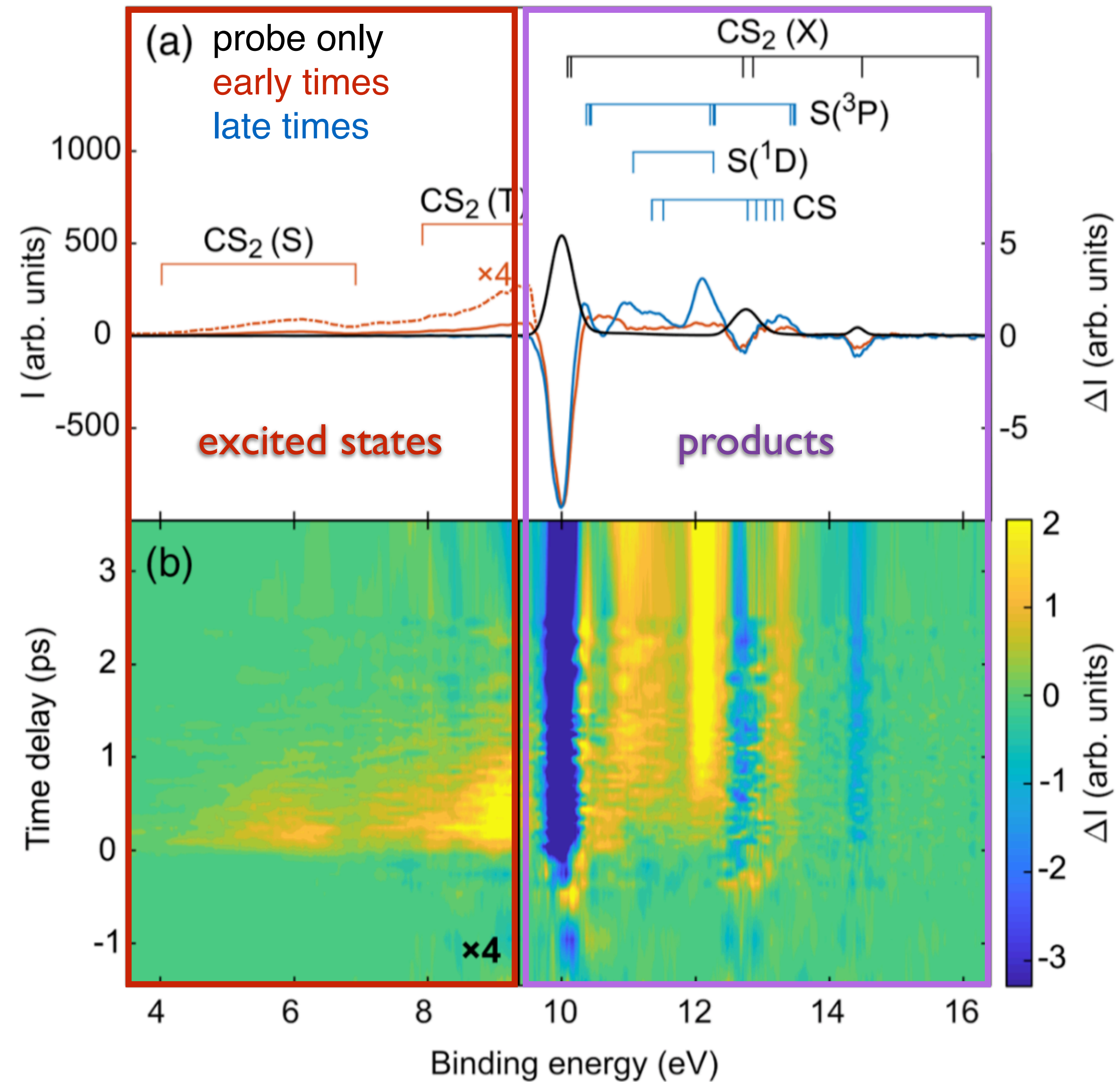
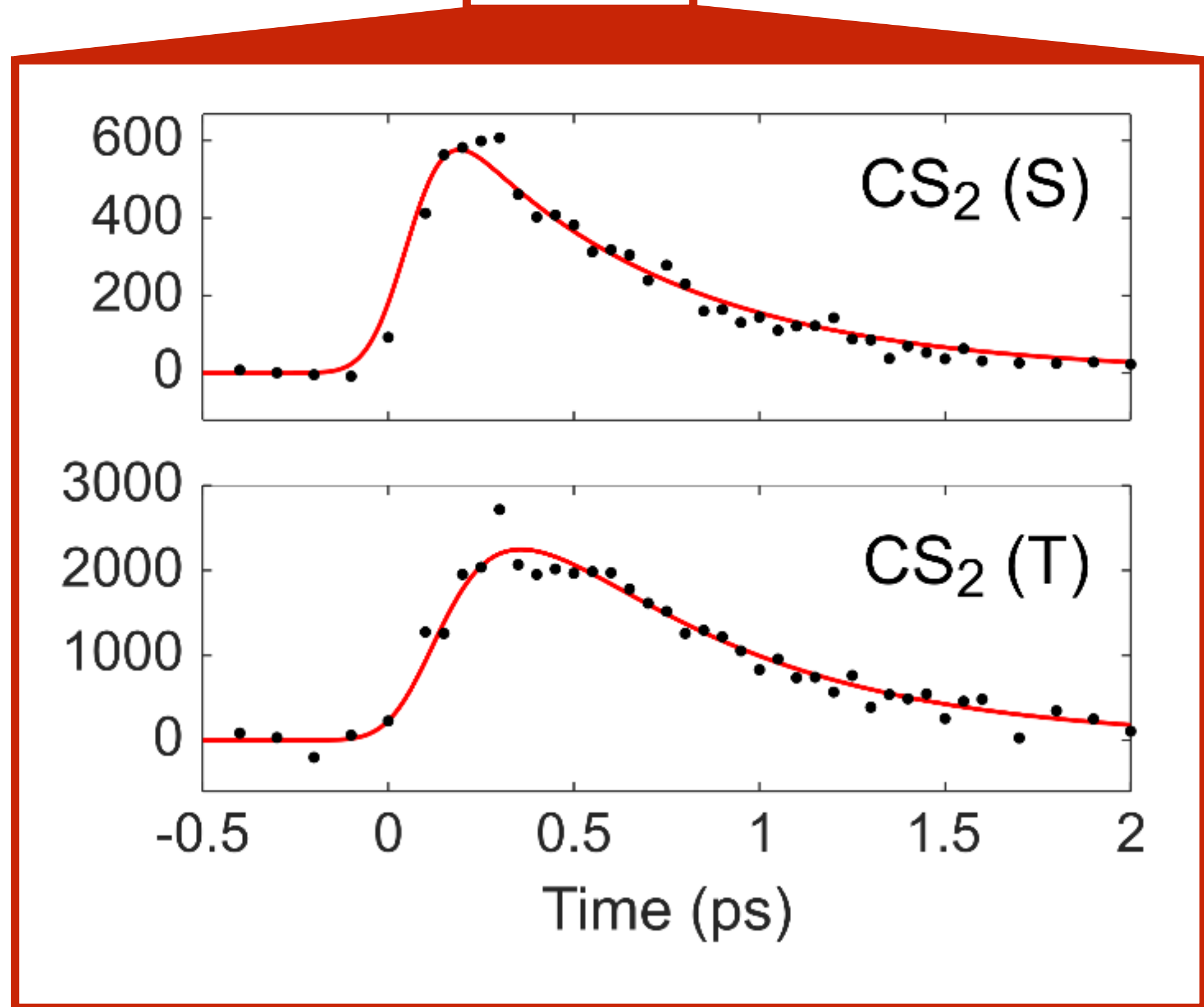
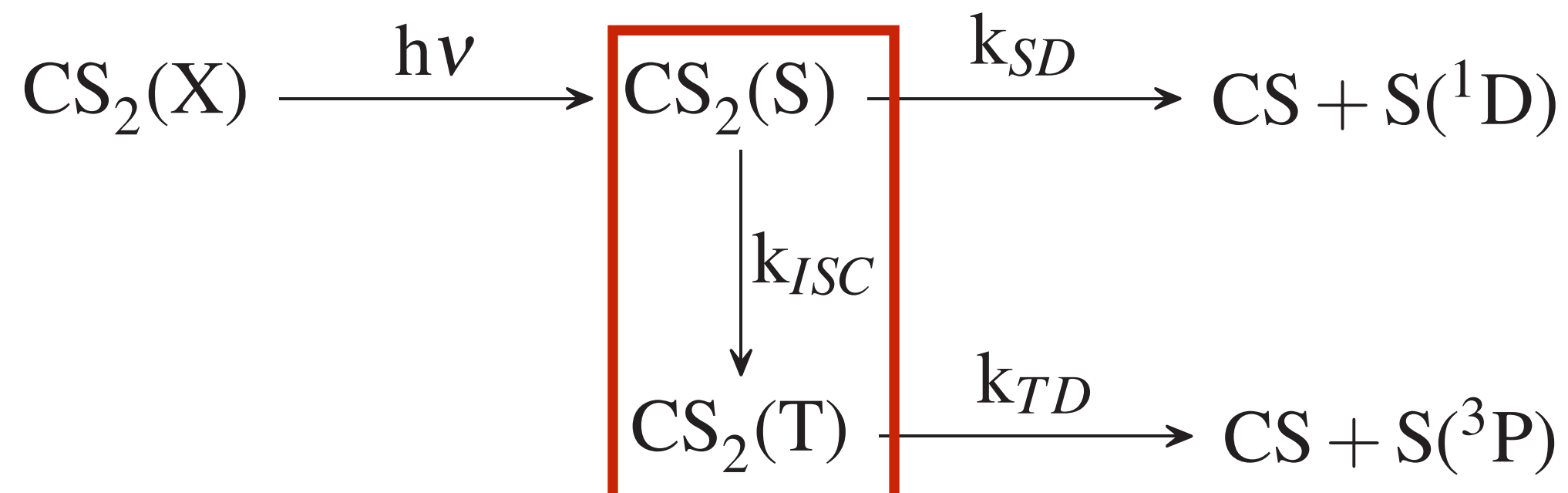
Mapping a complete photochemical reaction



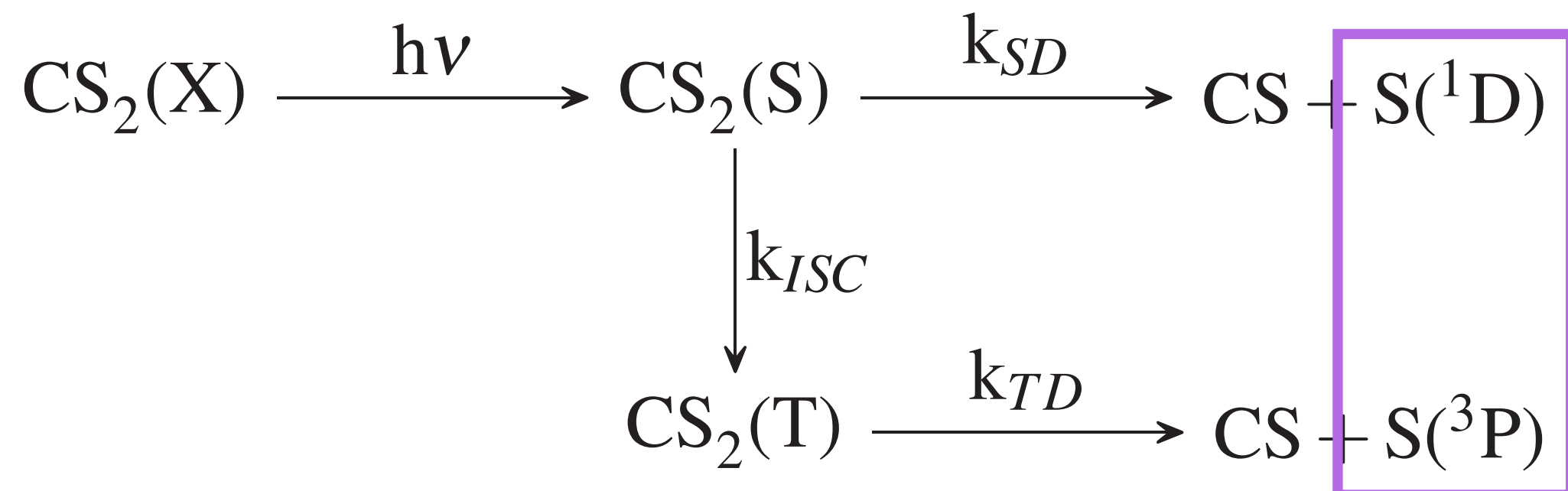
Mapping a complete photochemical reaction



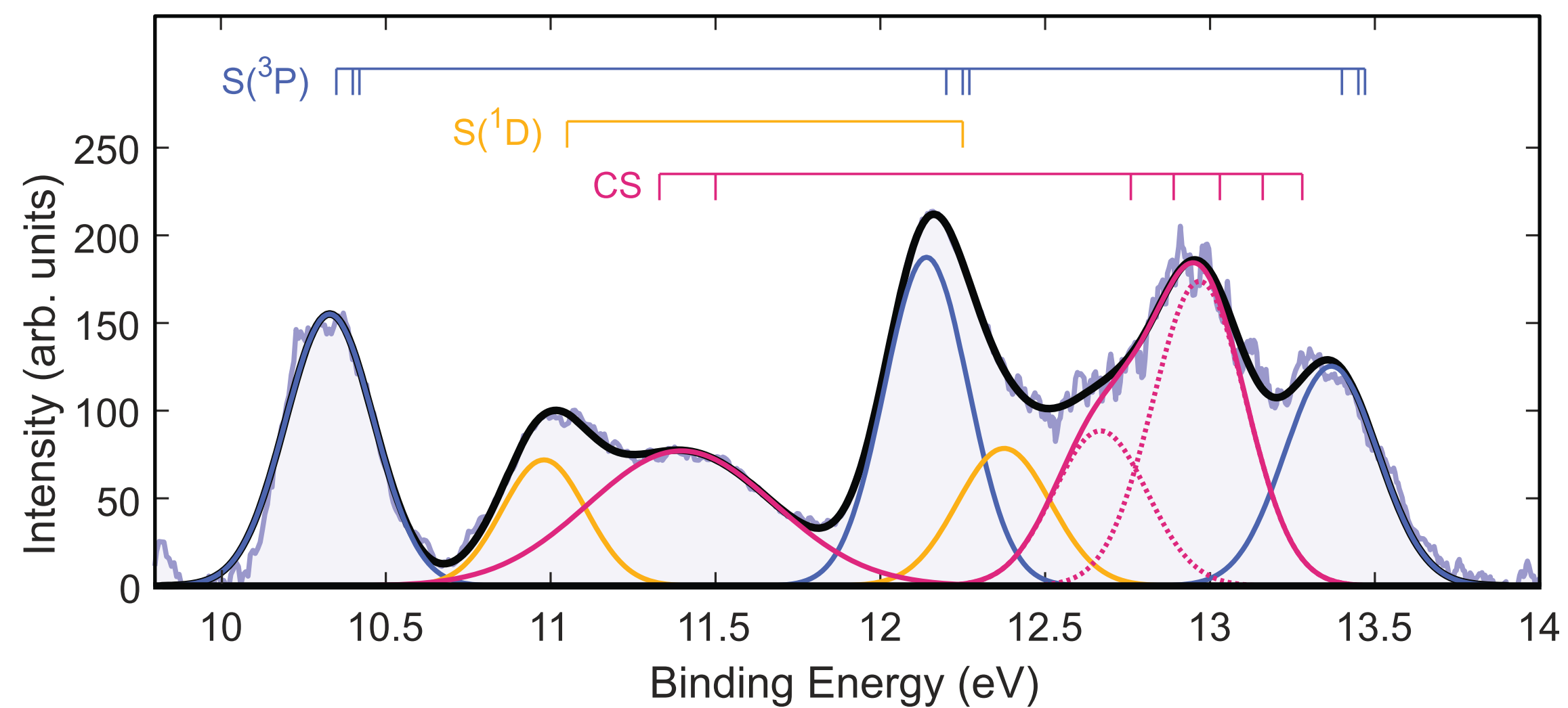
Mapping a complete photochemical reaction



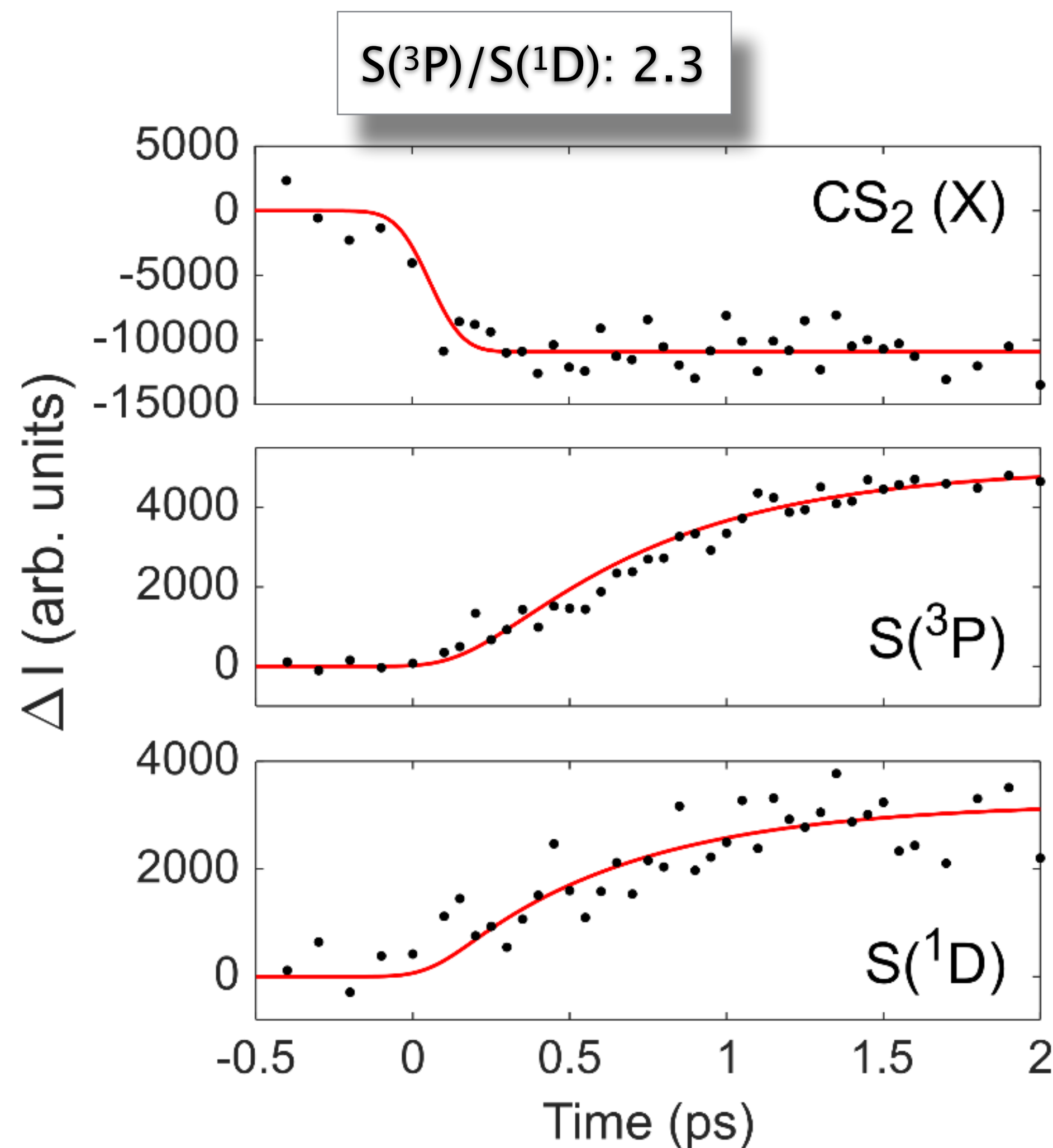
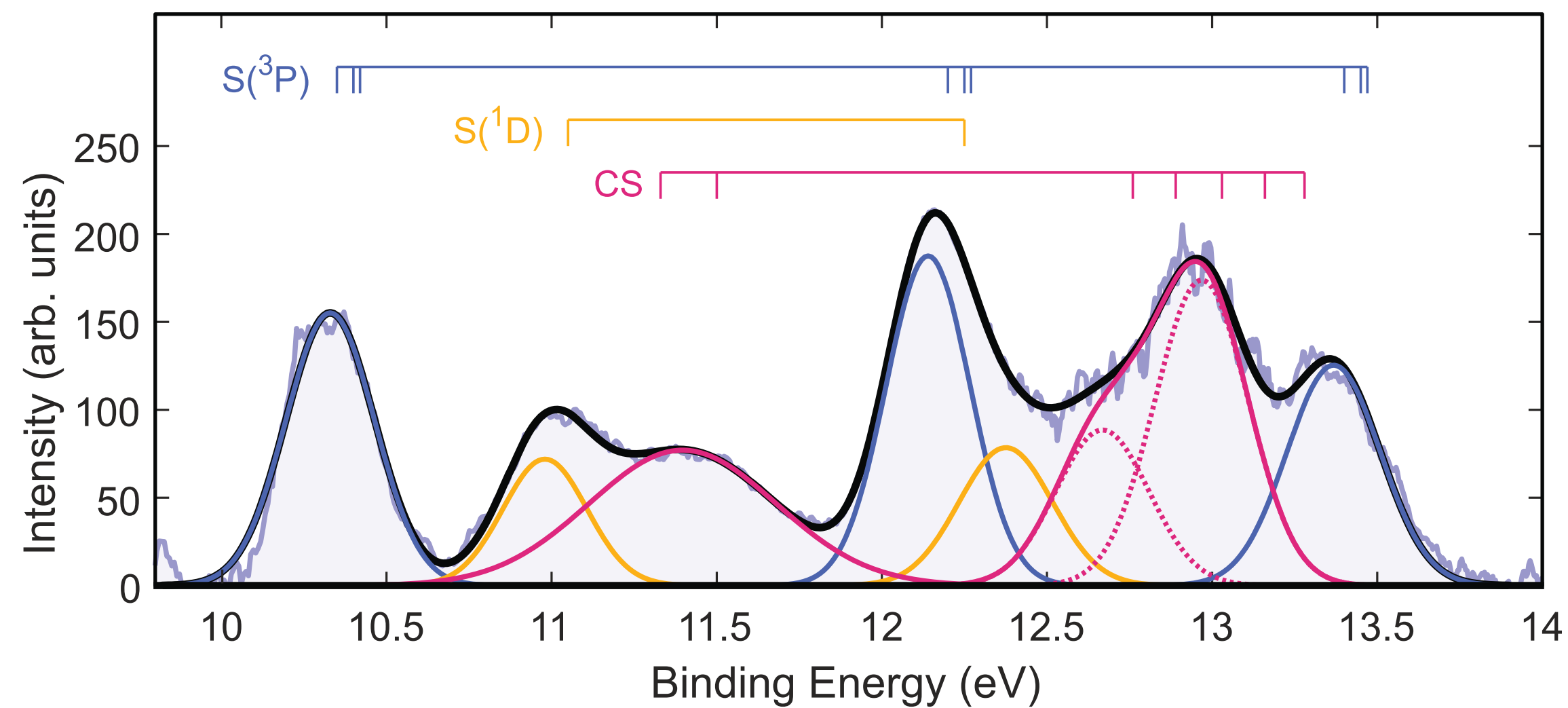
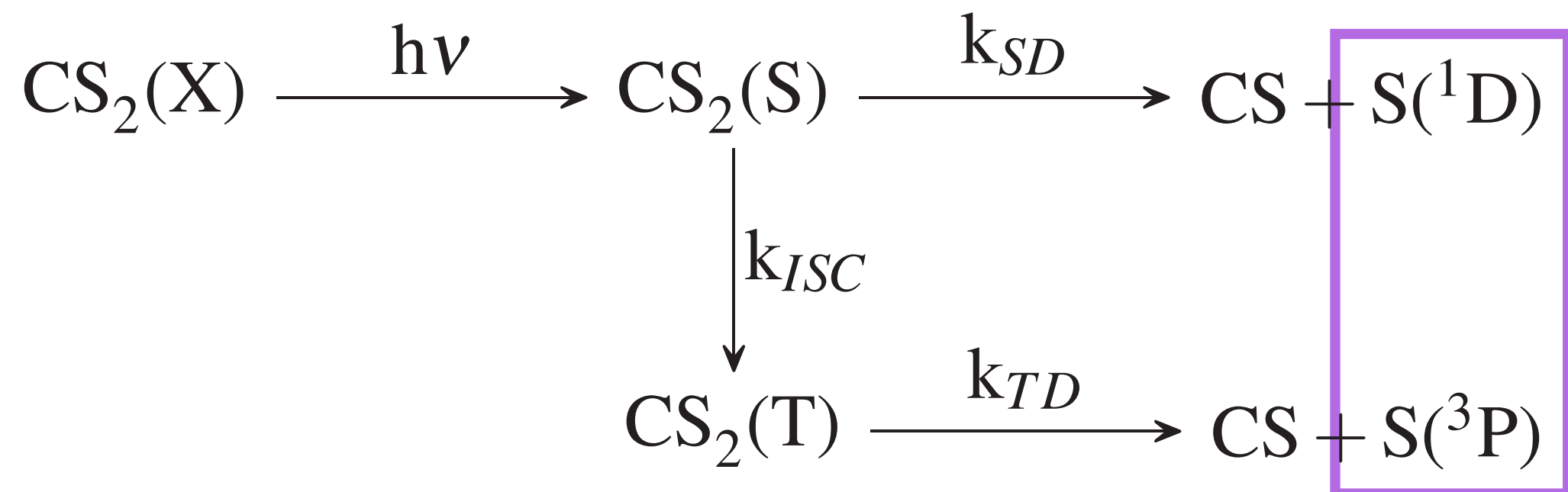
Mapping a complete photochemical reaction



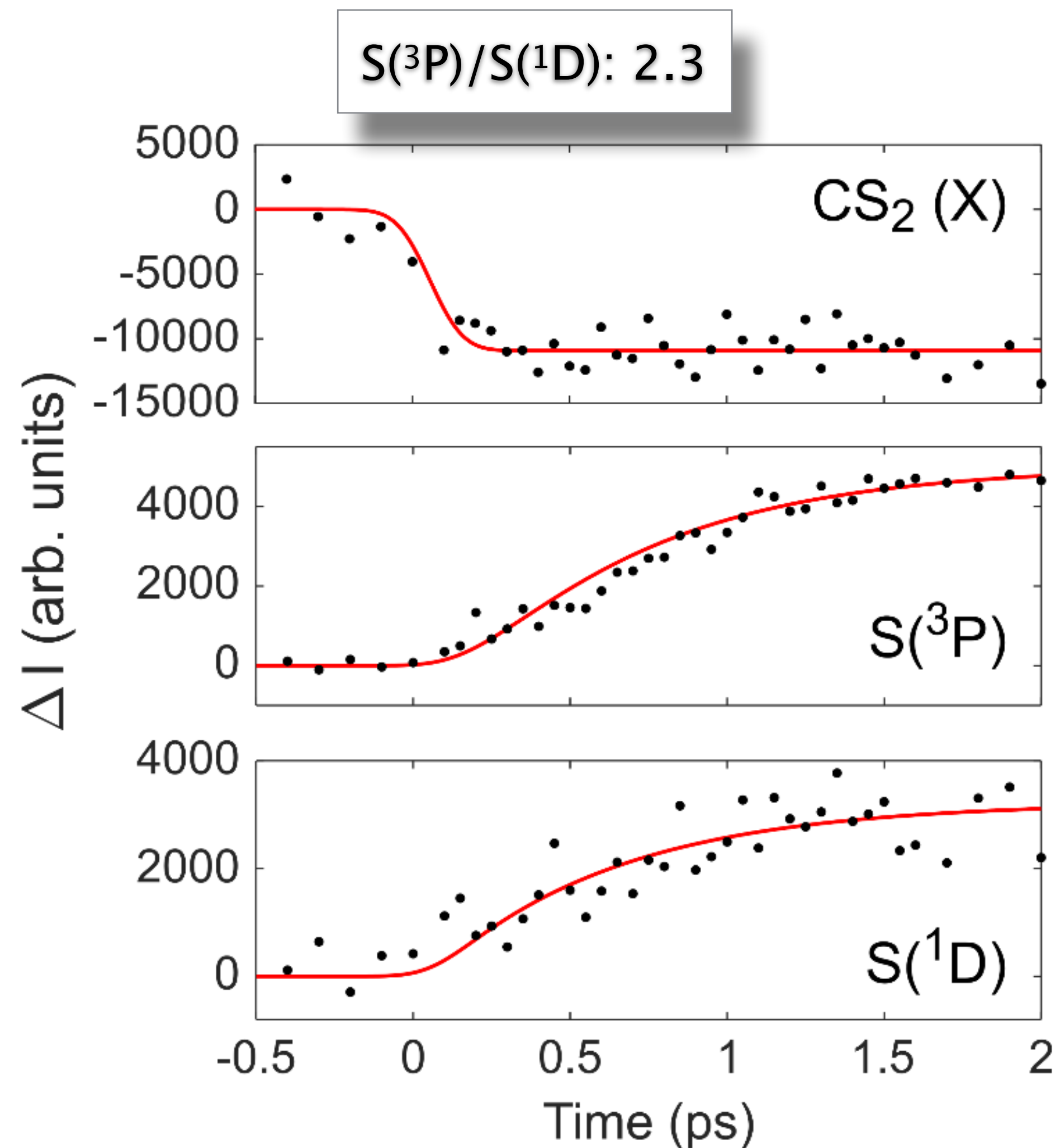
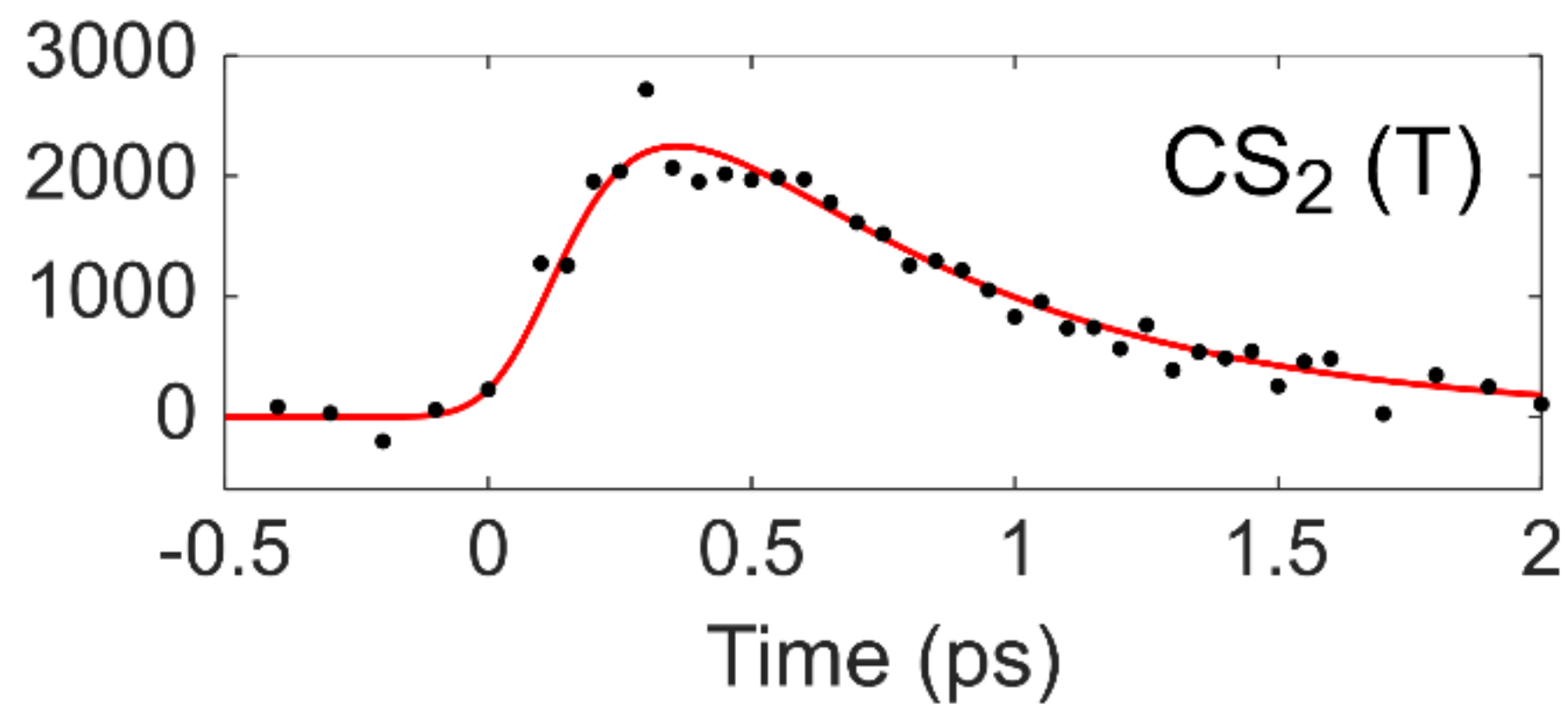
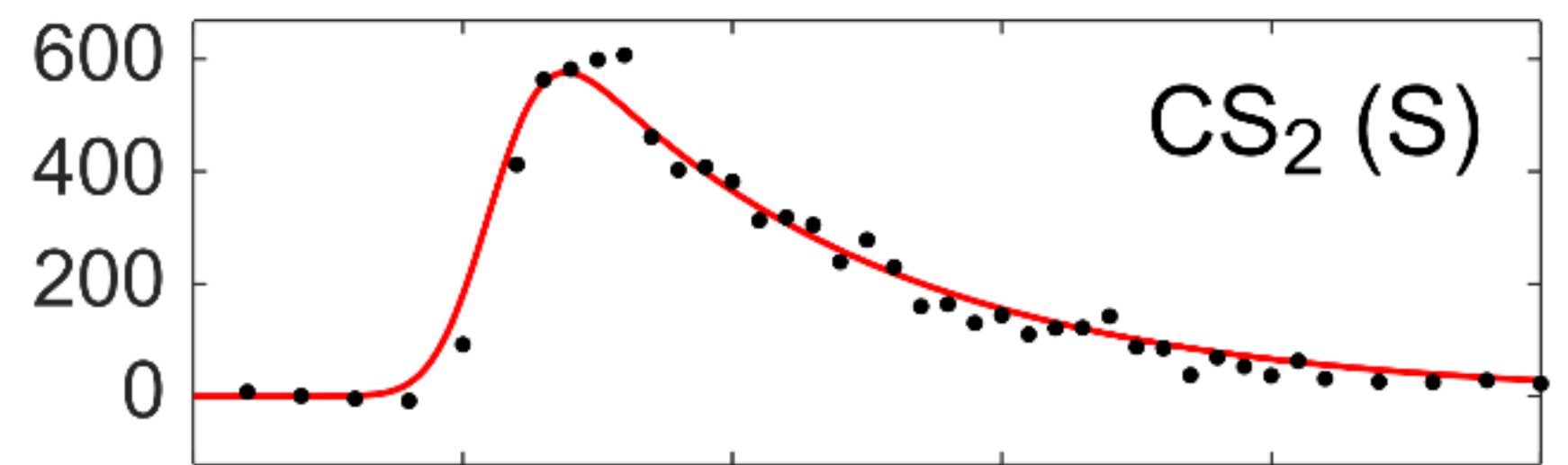
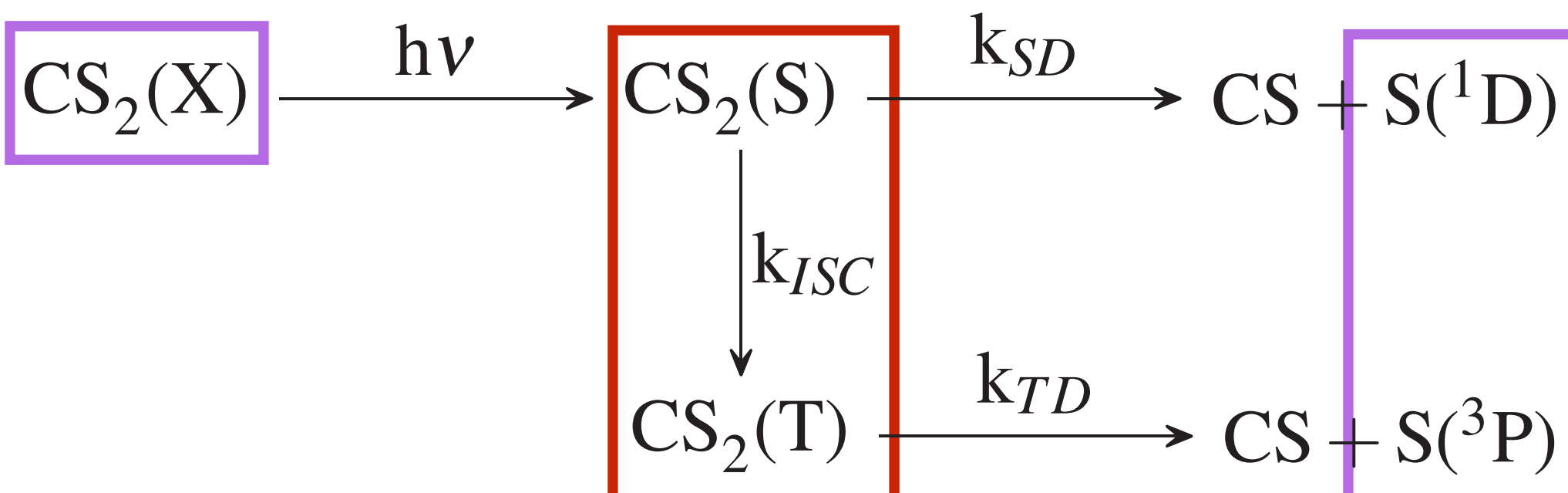
$\text{S}(^3\text{P})/\text{S}(^1\text{D}): 2.3$



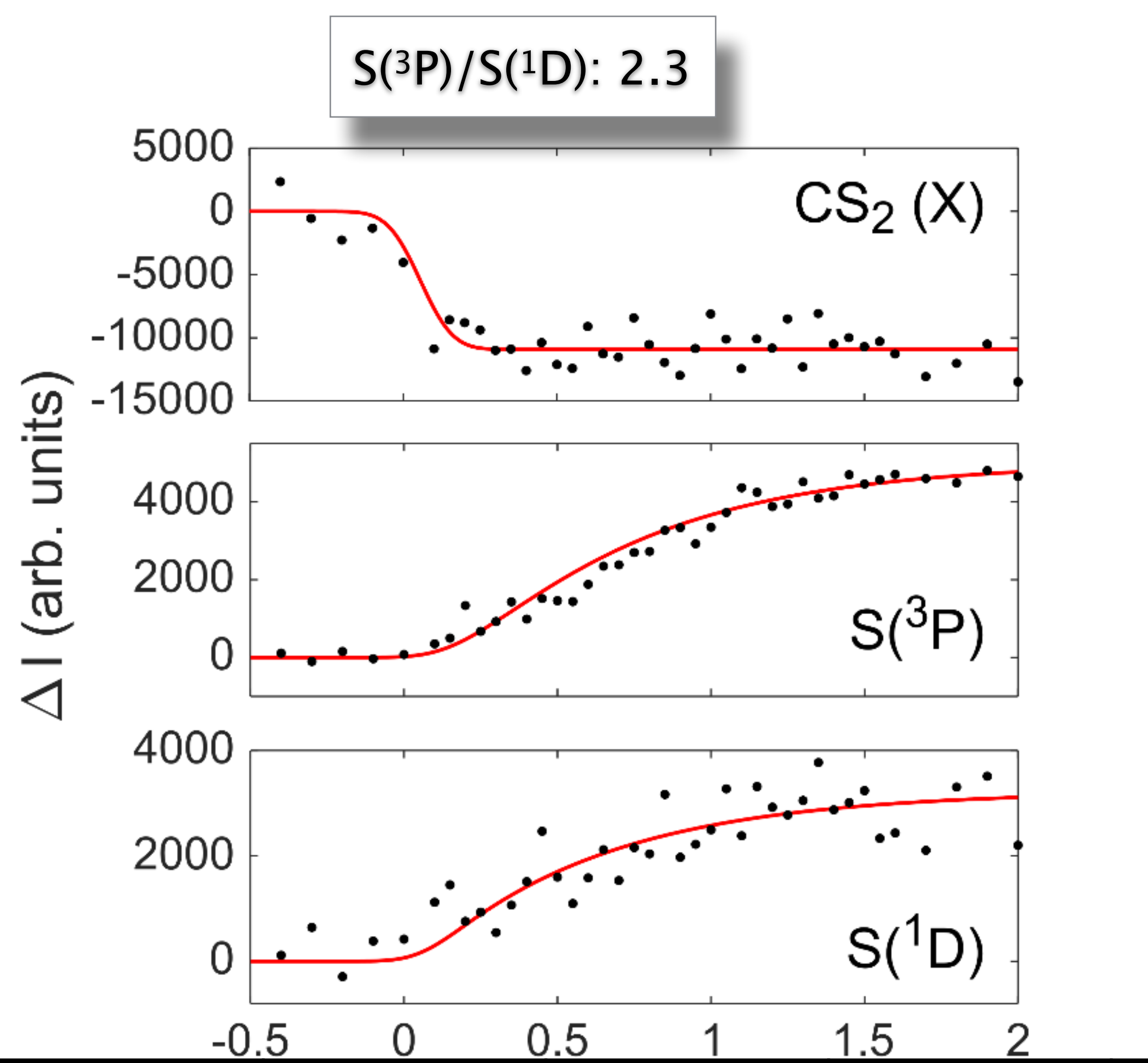
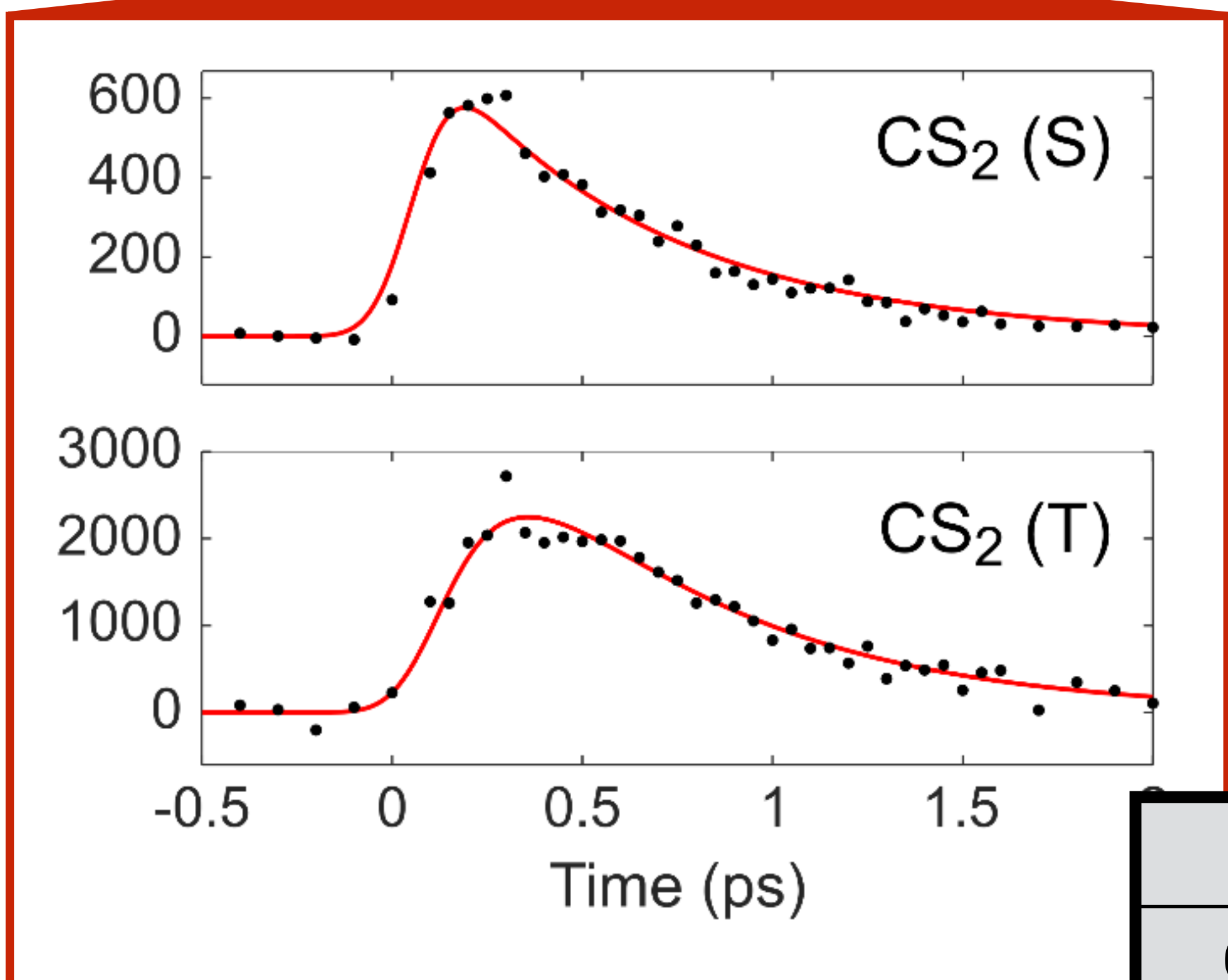
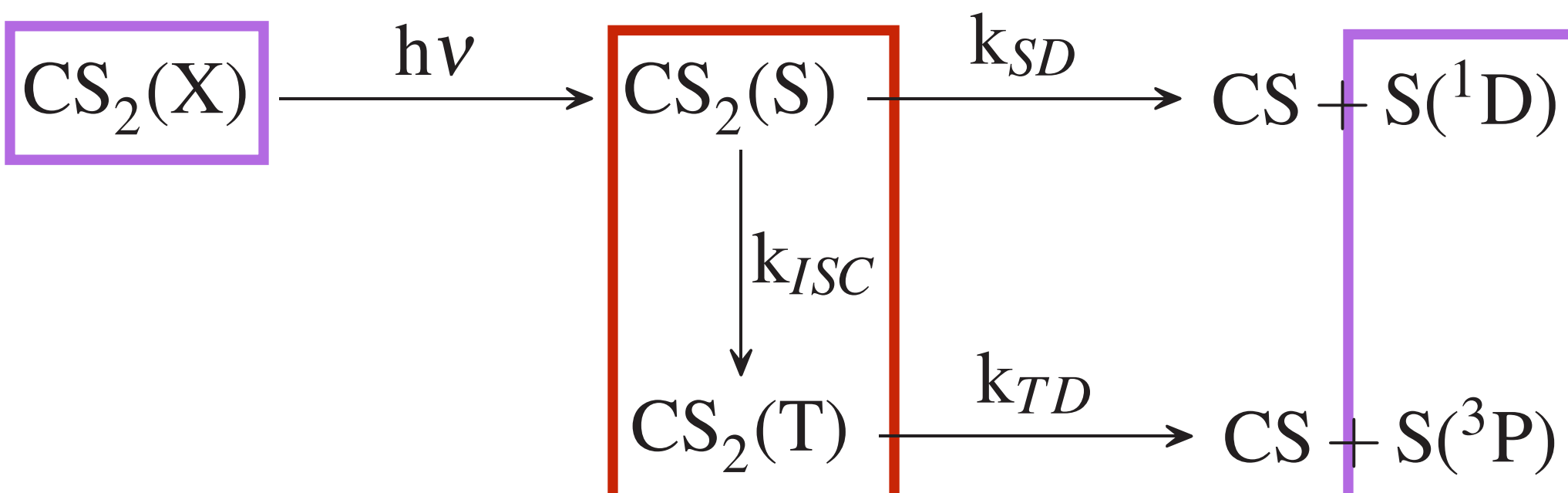
Mapping a complete photochemical reaction



Mapping a complete photochemical reaction



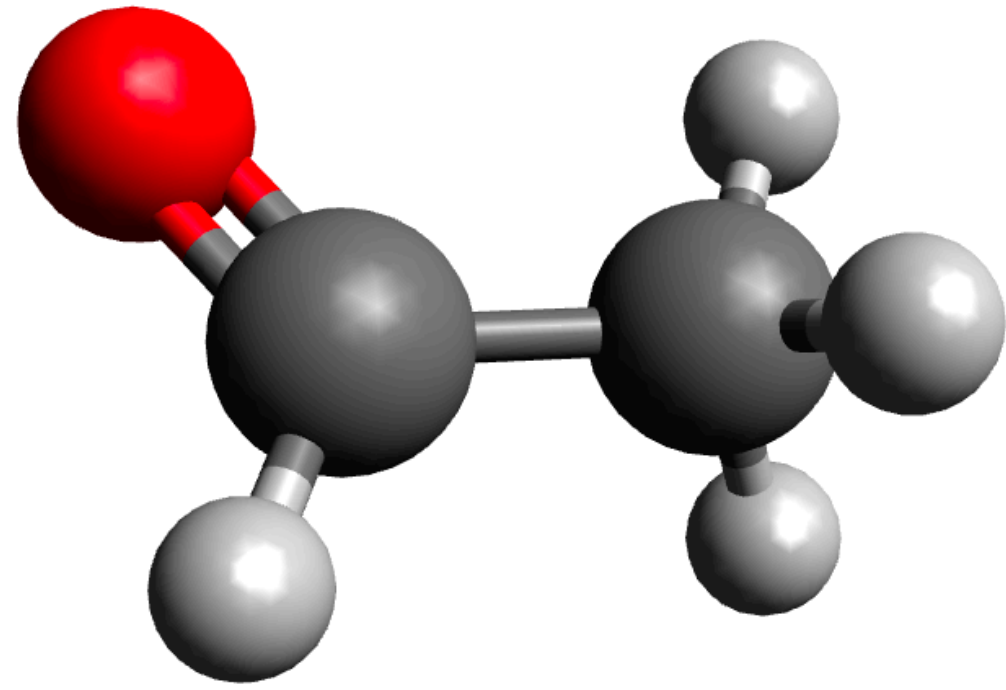
Mapping a complete photochemical reaction



τ_s	$T^{50\%}(\text{S})$	$T^{50\%}(\text{D})$	$\tau_{ISC}(1/k_{ISC})$	$\tau_{SD}(1/k_{SD})$	$\tau_{TD}(1/k_{TD})$
620 fs	520 fs	690 fs	890 fs	2.0 ps	180 fs

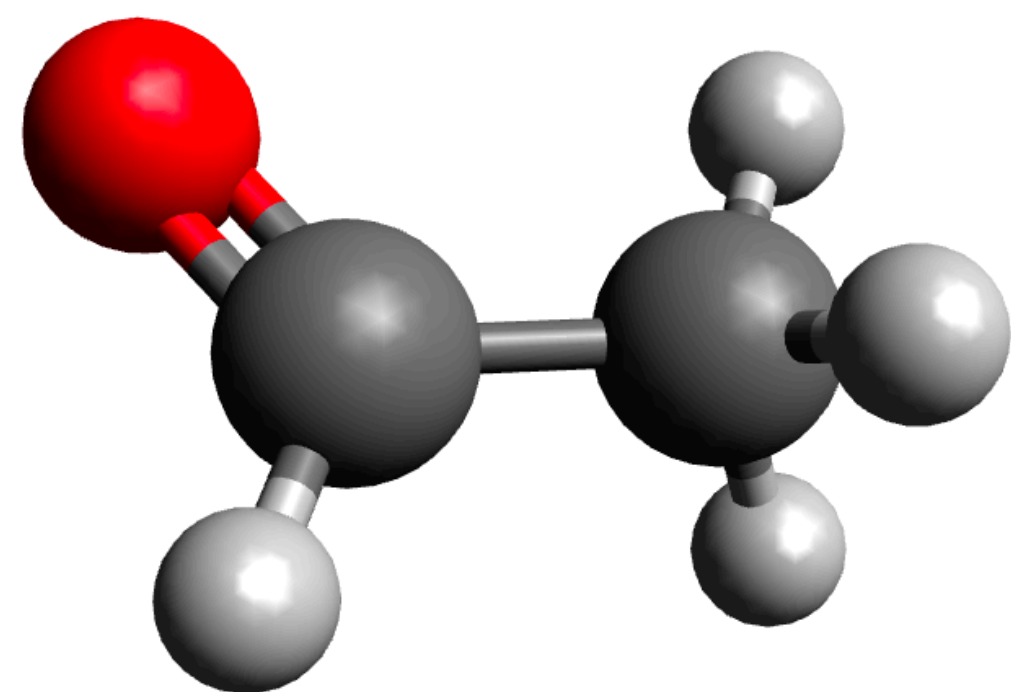


Outlook - Towards more complex photochemistry – *photodissociation of acetaldehyde: roaming dynamics(?)* –

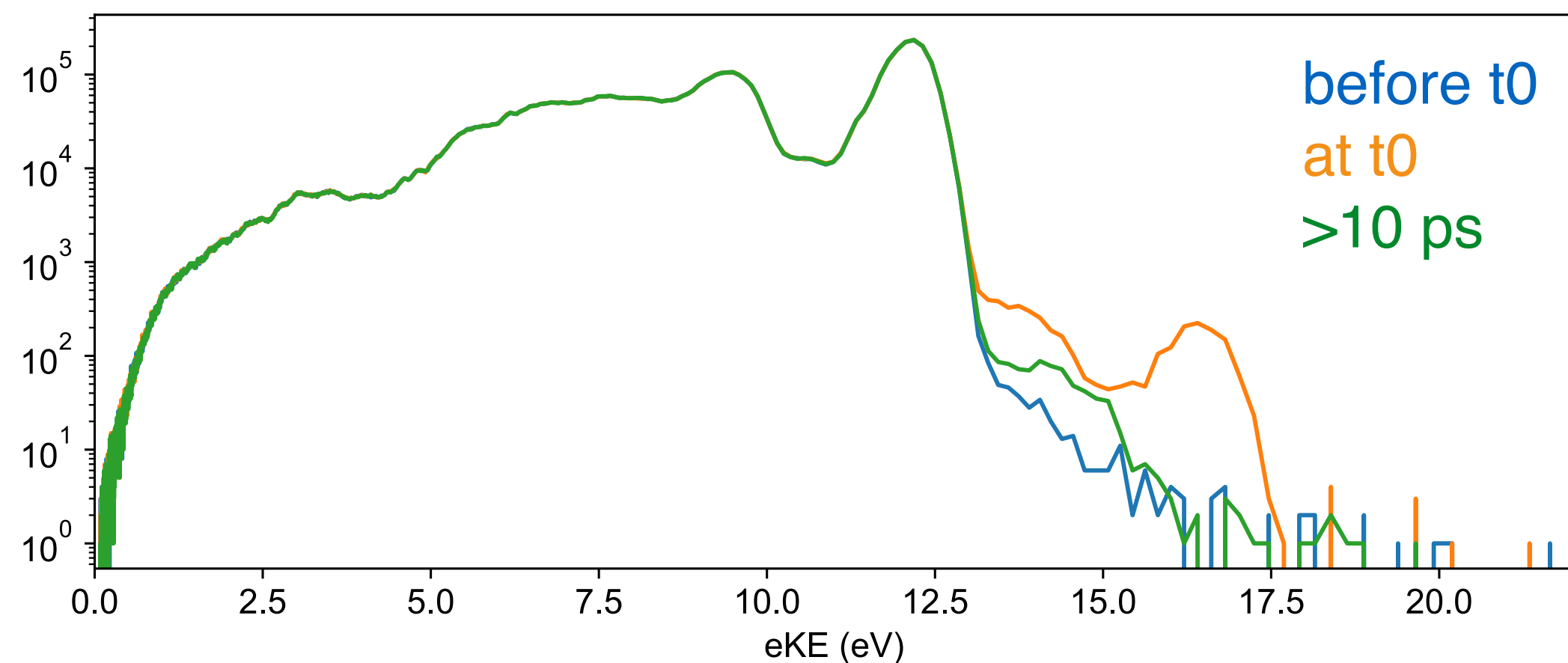


266 nm pump, 56nm probe

Outlook - Towards more complex photochemistry – *photodissociation of acetaldehyde: roaming dynamics(?)* –

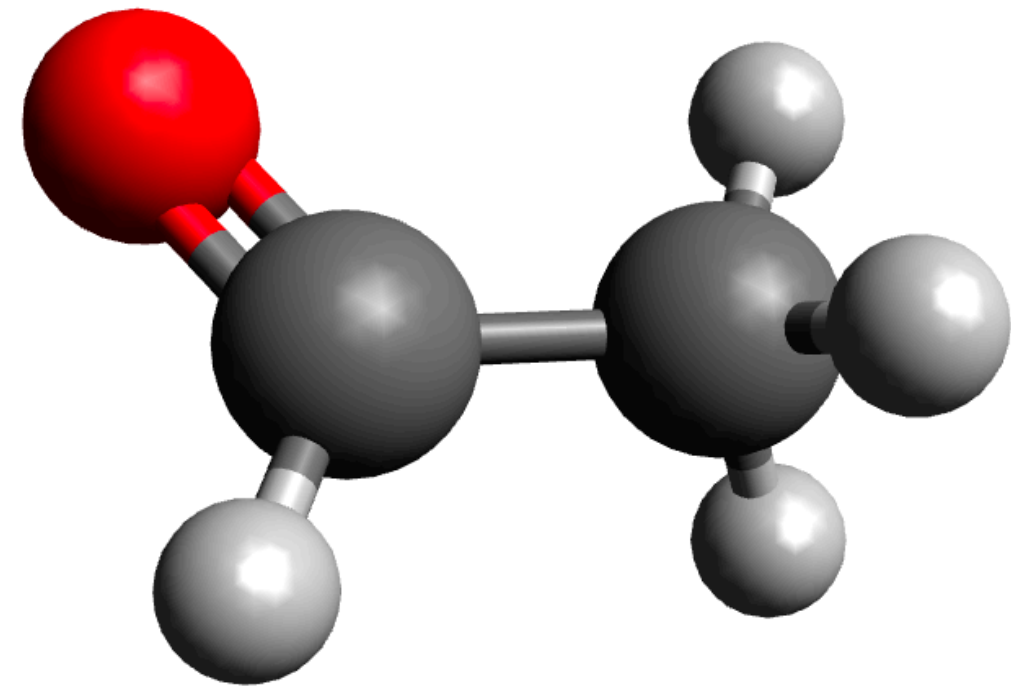


266 nm pump, 56nm probe

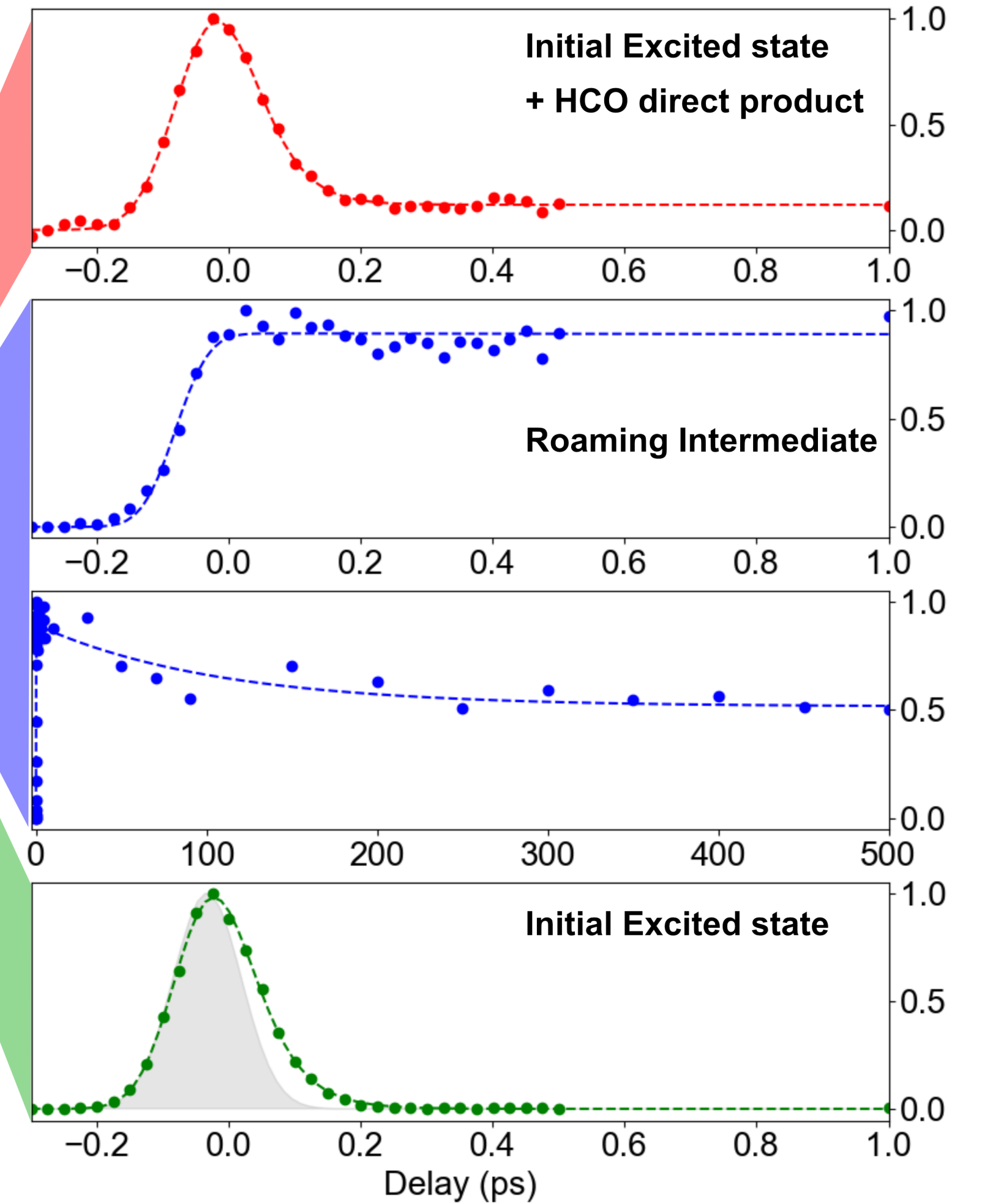
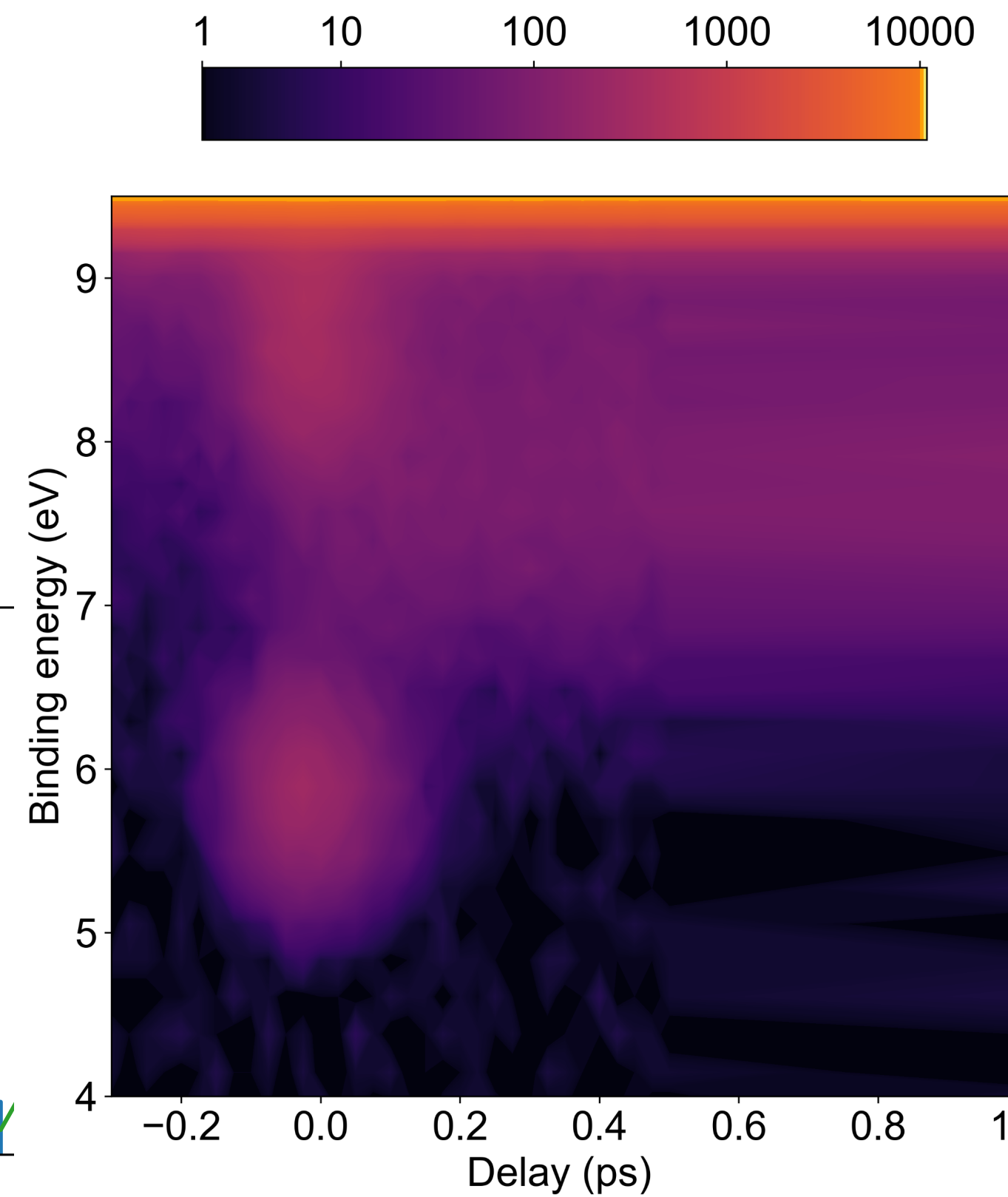
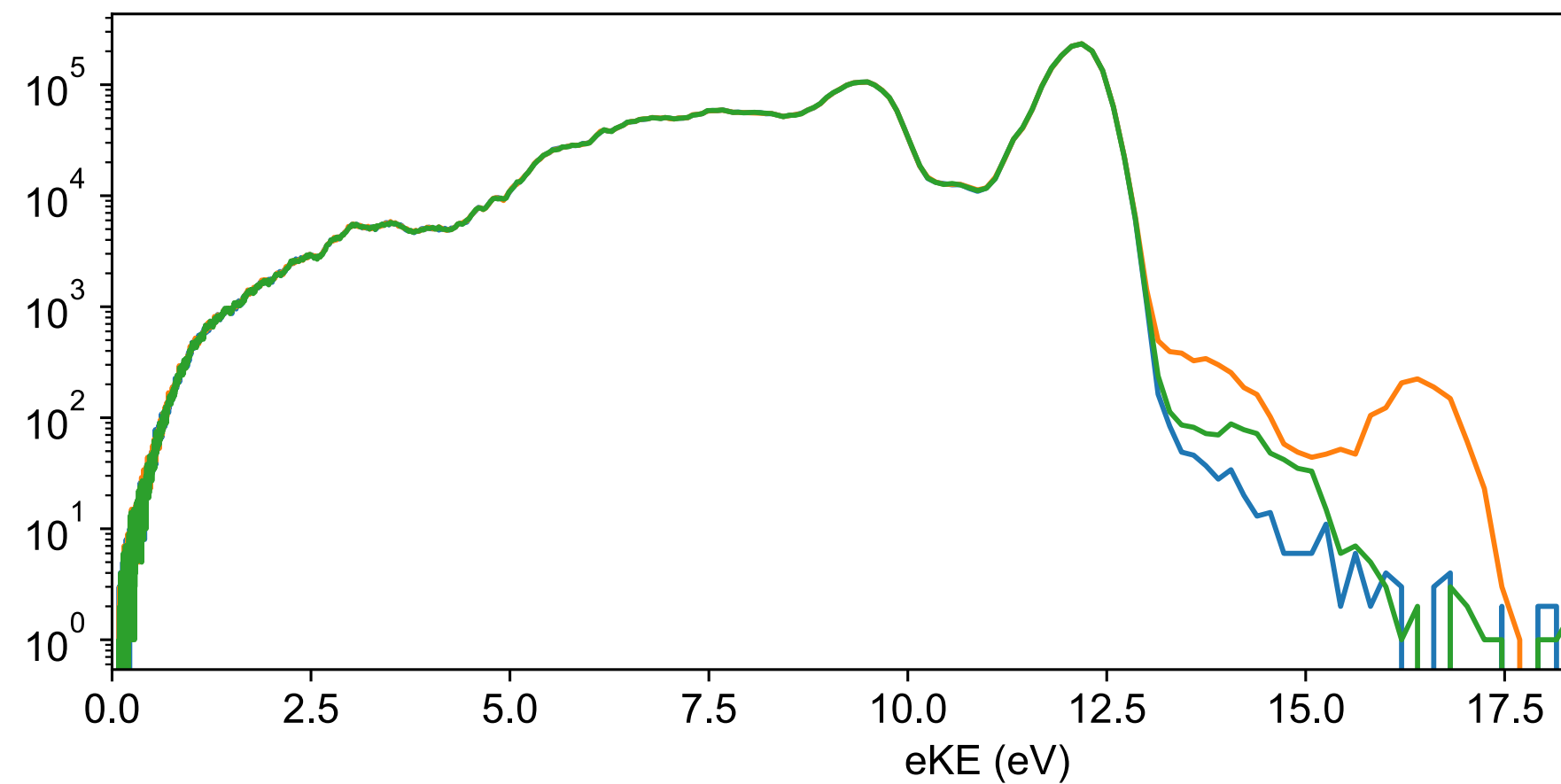


Outlook - Towards more complex photochemistry

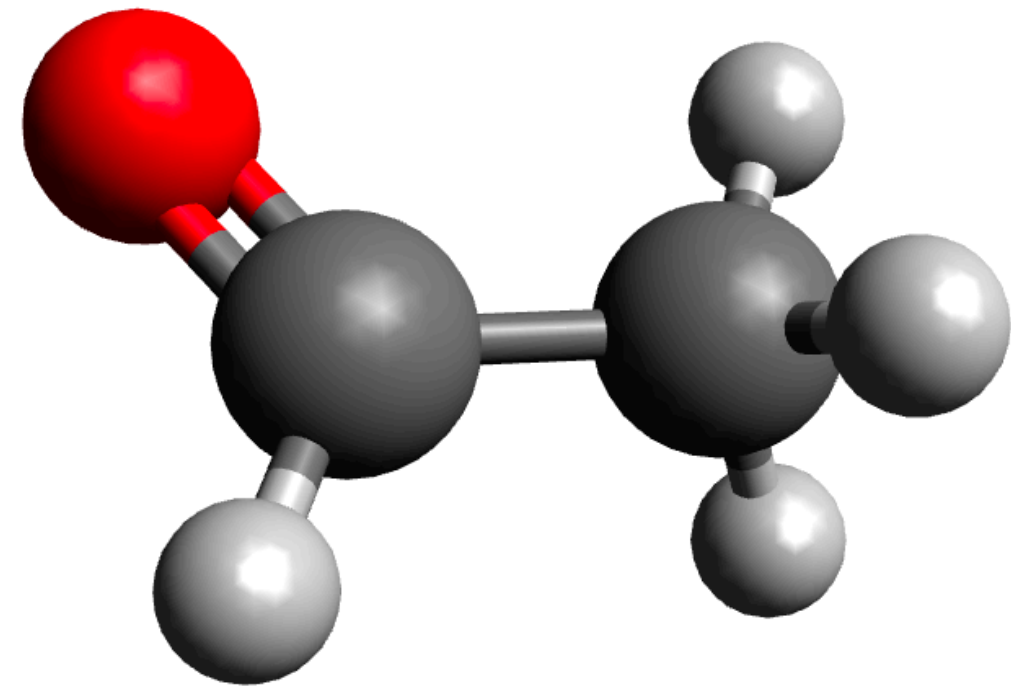
– photodissociation of acetaldehyde: roaming dynamics(?) –



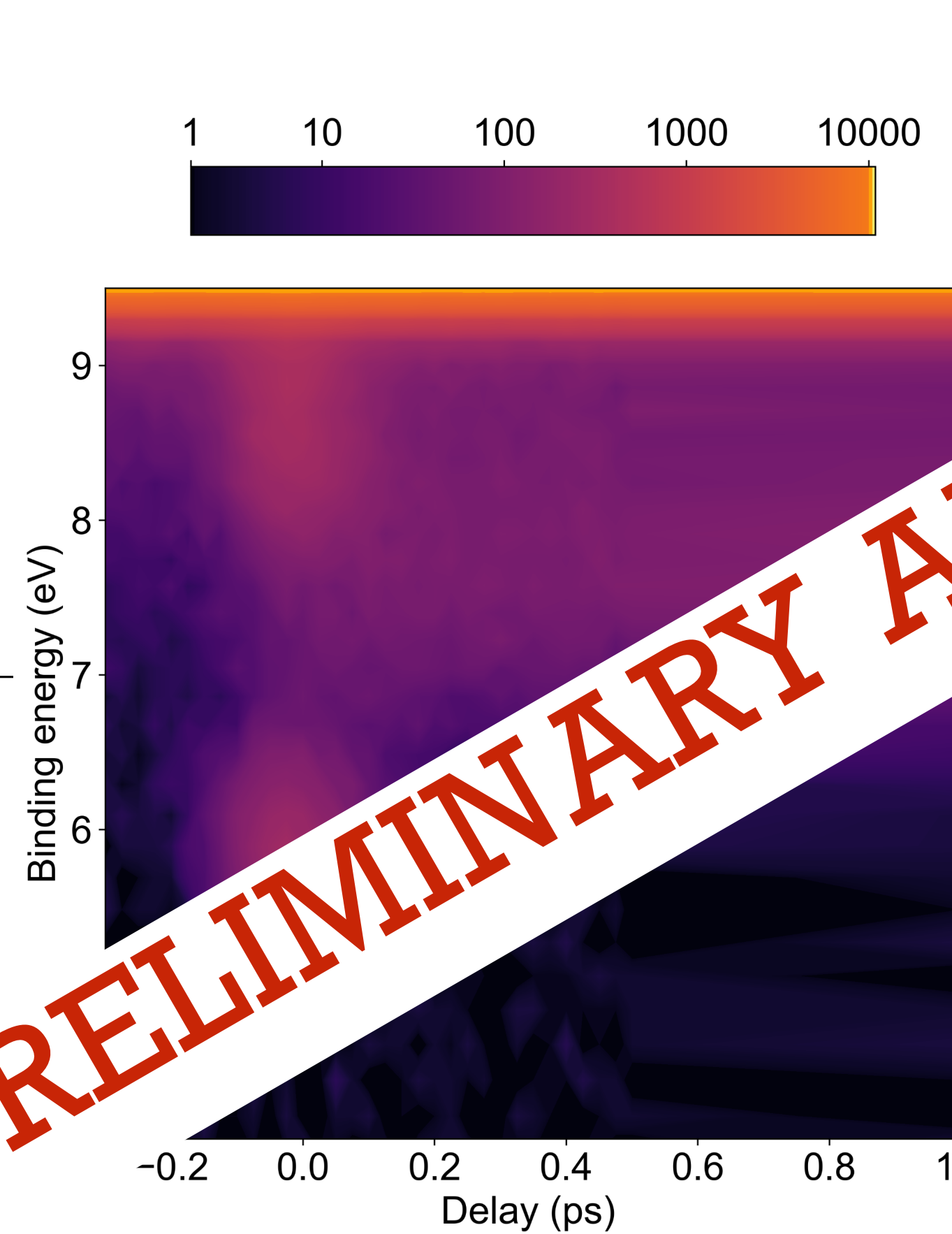
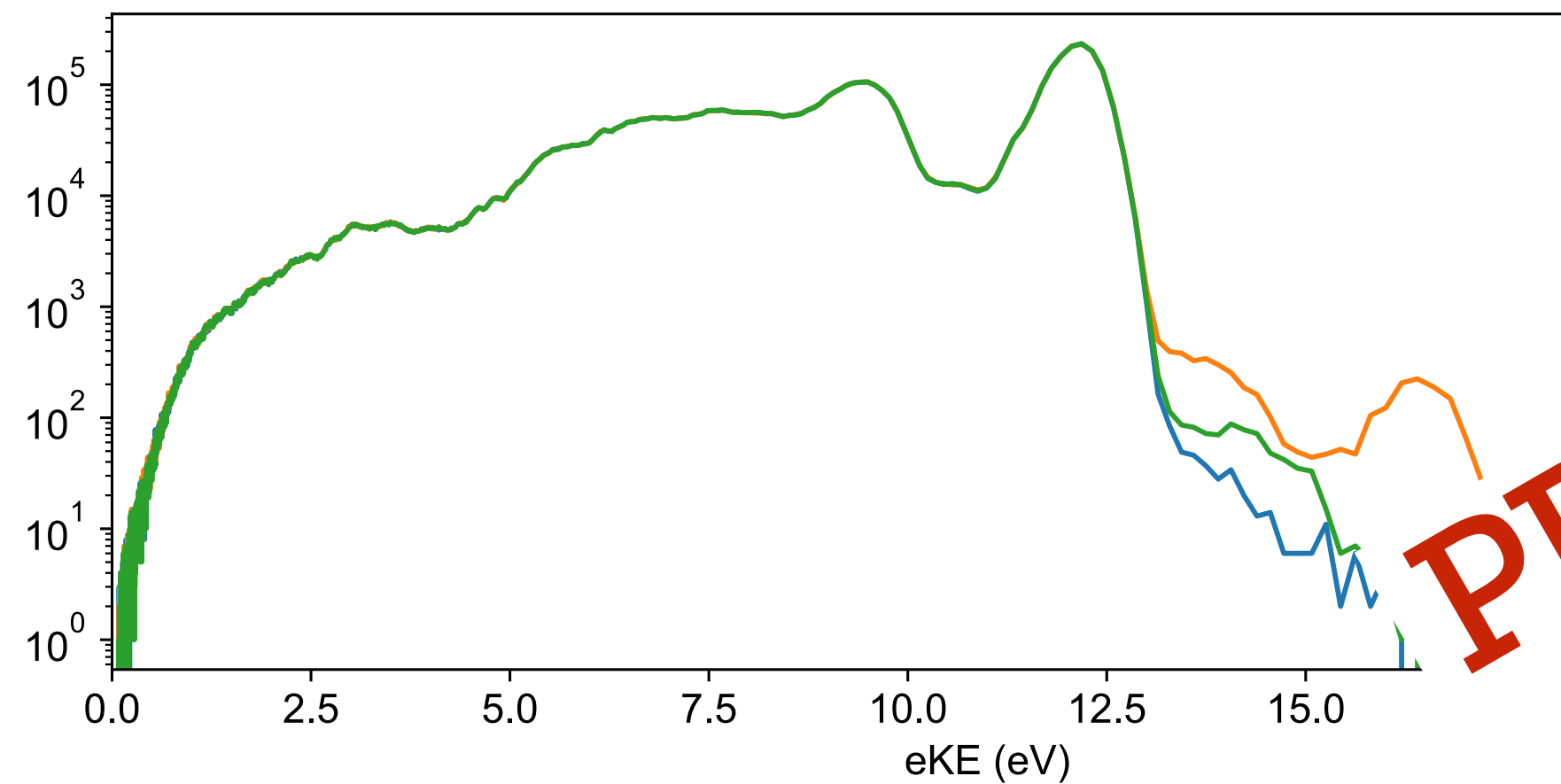
266 nm pump, 56nm probe



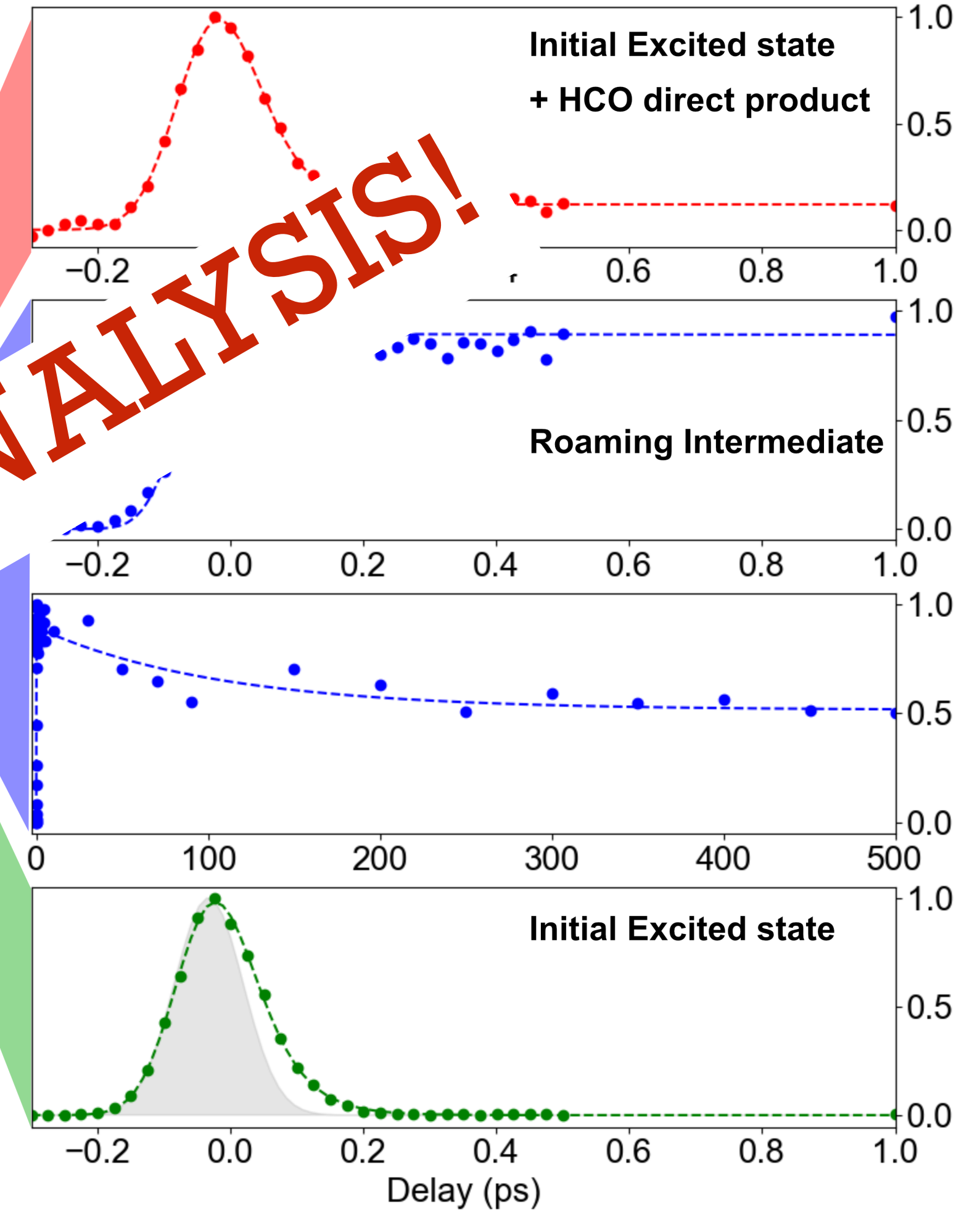
Outlook - Towards more complex photochemistry – photodissociation of acetaldehyde: roaming dynamics(?) –



266 nm pump, 56nm probe

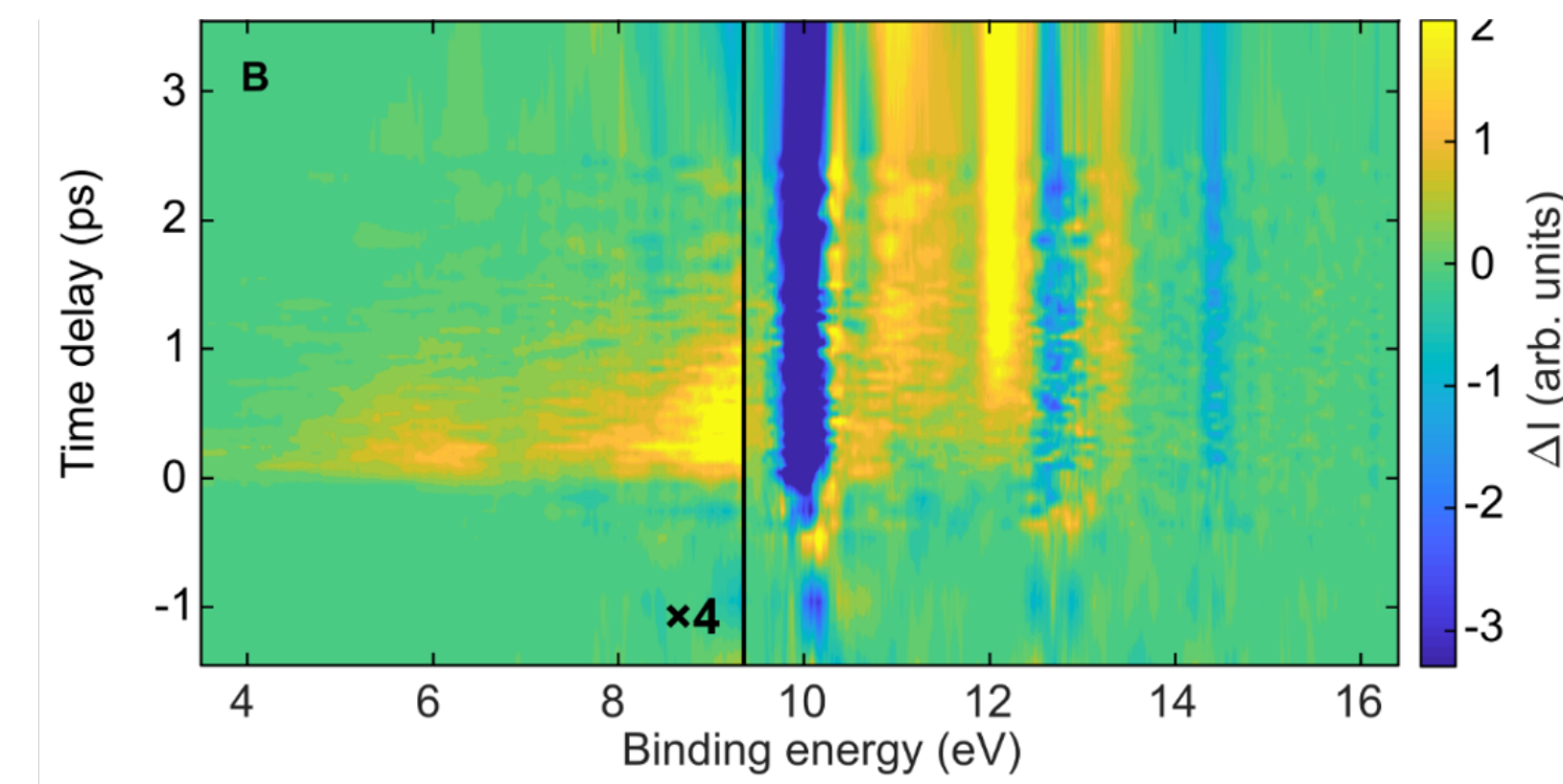


PRELIMINARY ANALYSIS!



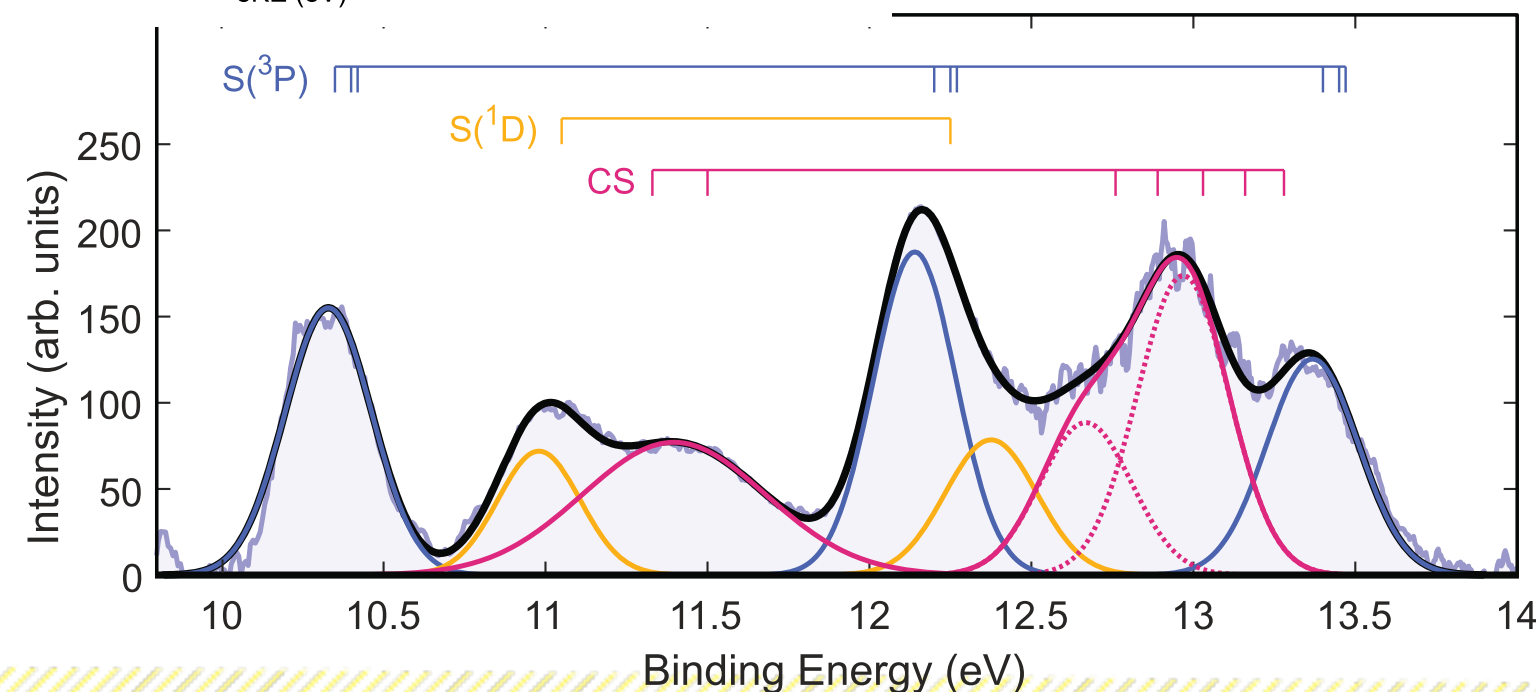
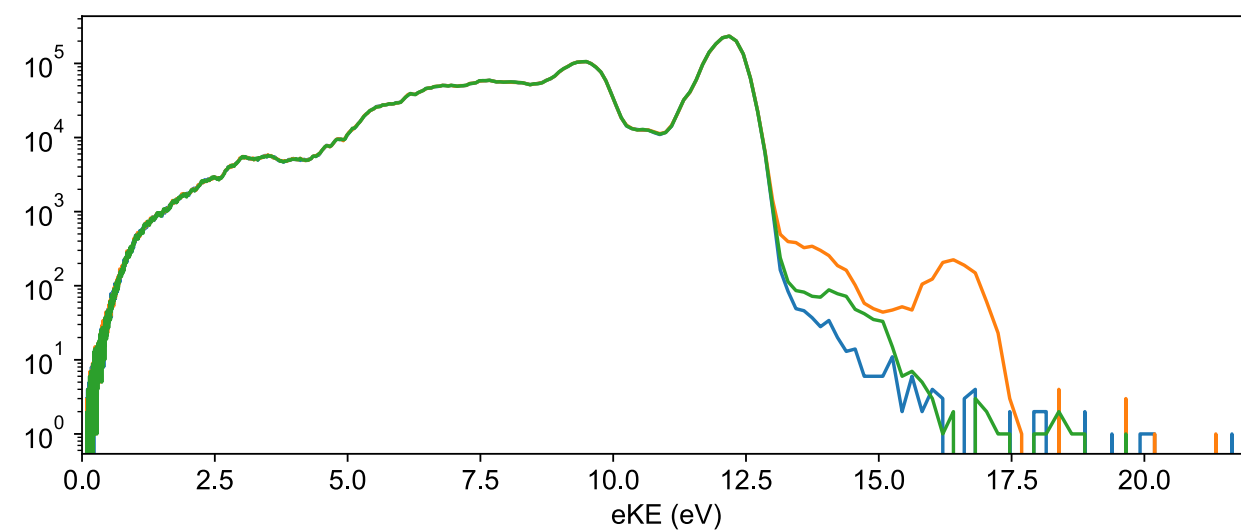
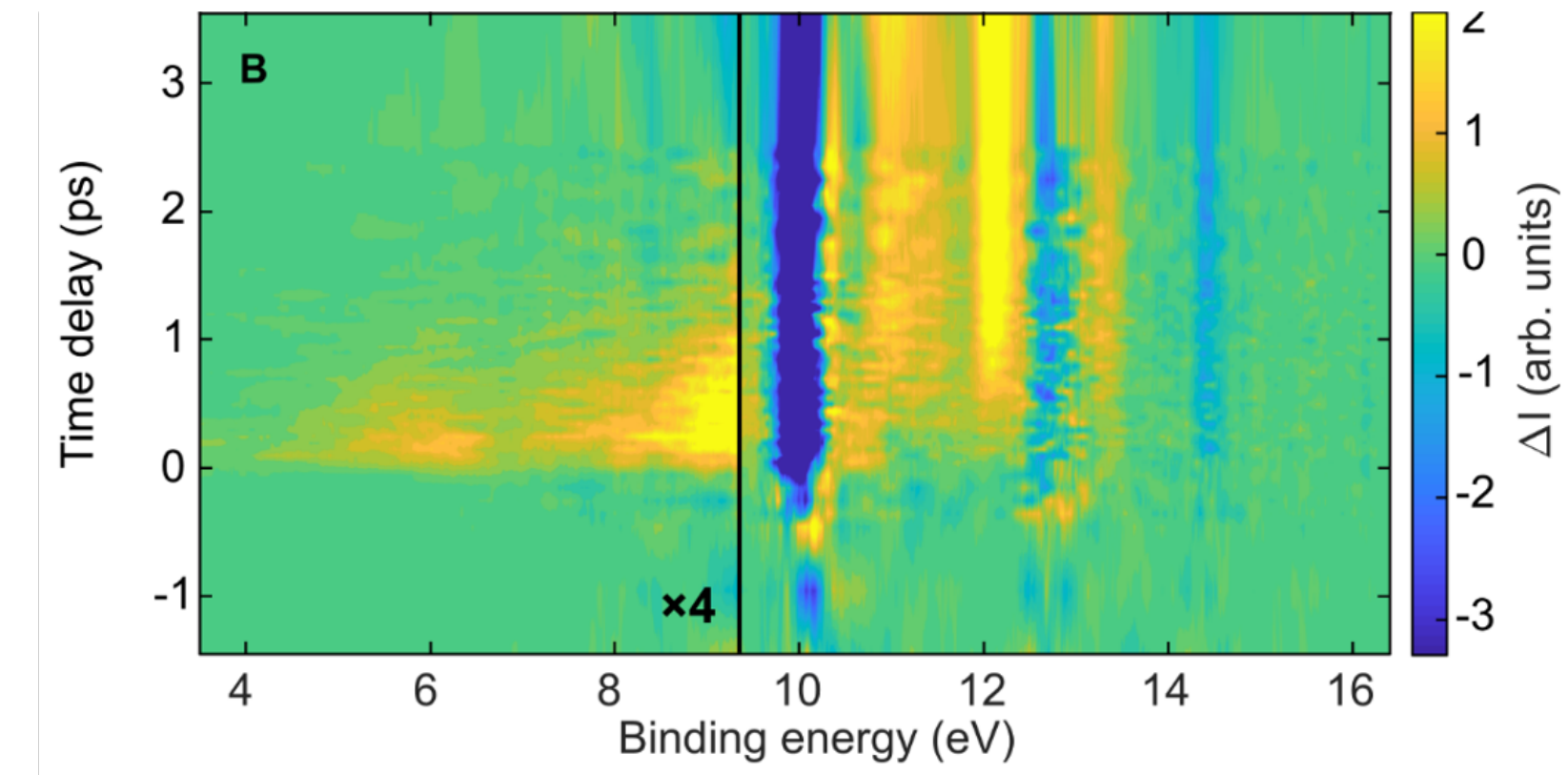
Conclusions

- UV-pump XUV-probe enables observation of complete photochemical reactions: reactants \rightarrow intermediates \rightarrow products
- For CS_2 photodissociation - ISC outcompetes singlet dissociation, with branching ratio 2.3:1 (triplet:singlet)
- Moving towards more complex photochemistry, first data on acetaldehyde dissociation



Conclusions

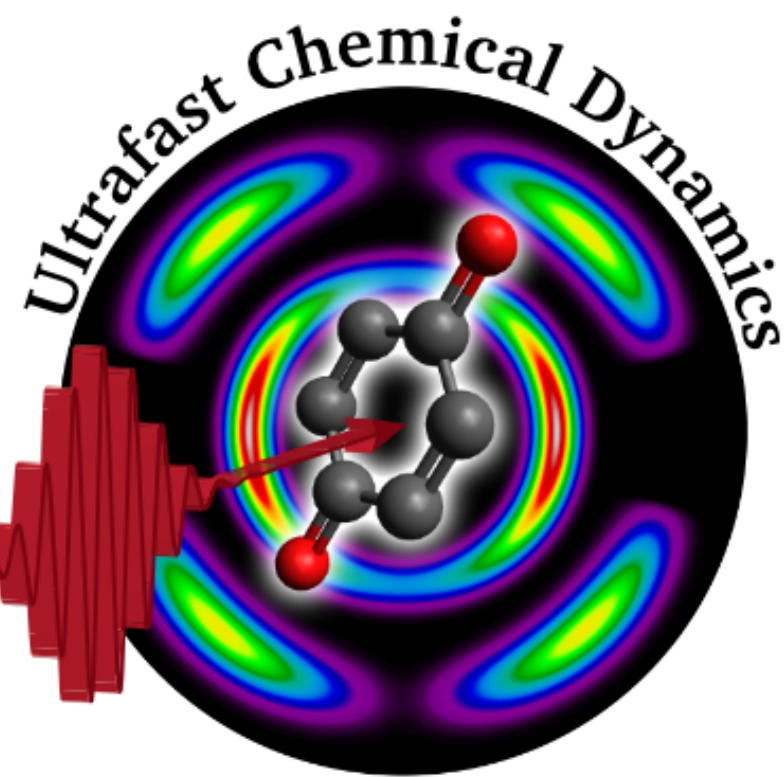
- UV-pump XUV-probe enables observation of complete photochemical reactions: reactants \rightarrow intermediates \rightarrow products
- For CS_2 photodissociation - ISC outcompetes singlet dissociation, with branching ratio 2.3:1 (triplet:singlet)
- Moving towards more complex photochemistry, first data on acetaldehyde dissociation



- Signals are small and on large background, due to low levels of excited state population and limited XUV flux
- Spectra are congested (even worse for larger systems...)
- Calculations at the required accuracy (including observables) are increasingly important.

Acknowledgements

The Horke Research group.



Institute for
Molecules and Materials
Radboud University



Grite Abma
Ana Caballo
Siwen Wang
Peter Krüger
Olga Duda
Saskia Pieters

Spectroscopy of Cold Molecules Department
Prof. Bas van de Meerakker

Administrative support
Marian de With

Technical support
André van Roij
Michiel Balster
Niek Janssen



Russell Minns
Adam Smith
Emily M. Warne
Weronika Razmus



Adam Kirrander
Darren Bellshaw
Maria Tudorovskya



Science & Technology Facilities Council
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Emma Springate
Richard T. Chapman
Alfred J. H. Jones
Cephise Cacho



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