Attosecond momentum-resolved resonant inelastic X-ray scattering of photo-excited molecules

NICE 2026

Nonlinear Imaging and Coherent Effects

Brandenburgische Technische Universität Cottbus - Senftenberg

Maksim Radionov (Gorelova's group)

Cat
&
tree

Attosecond time resolution

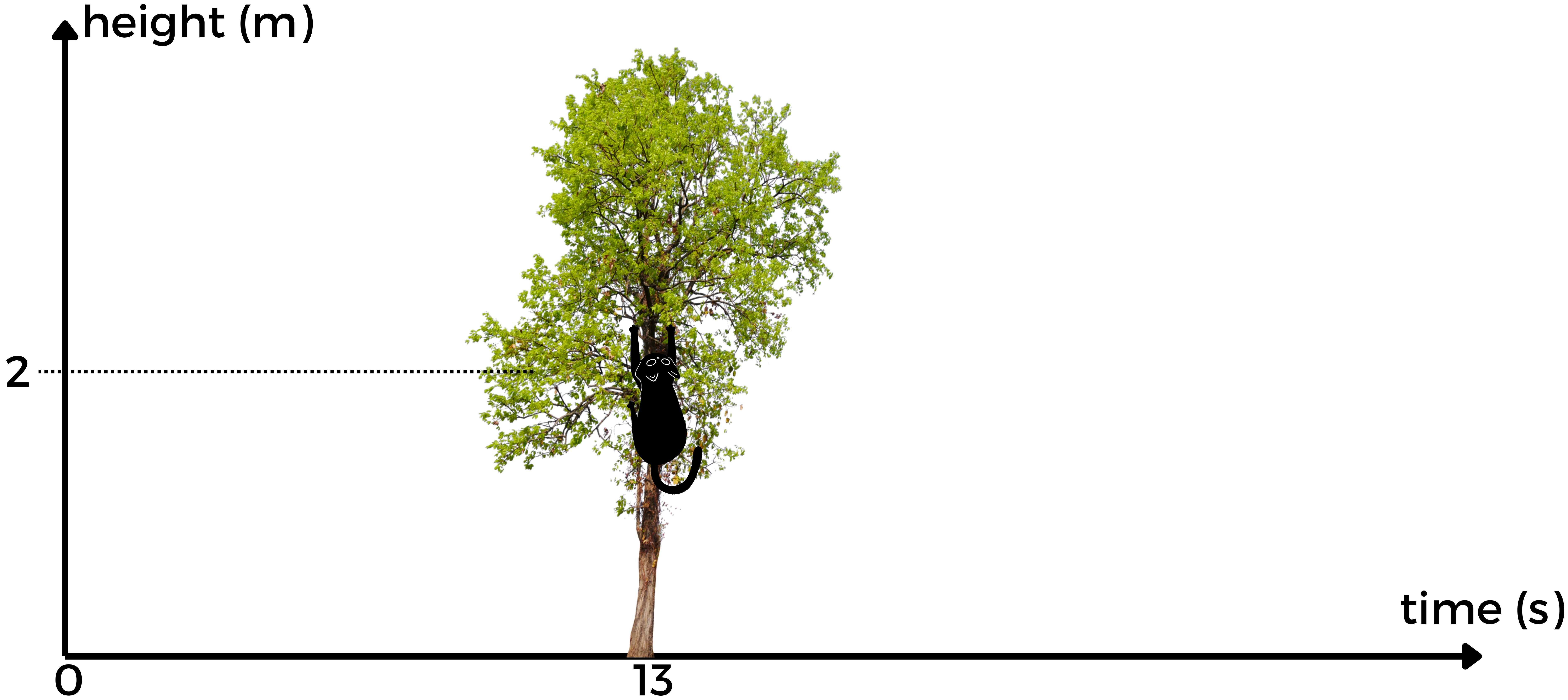
height (m)

We take photos of the cat on the tree.

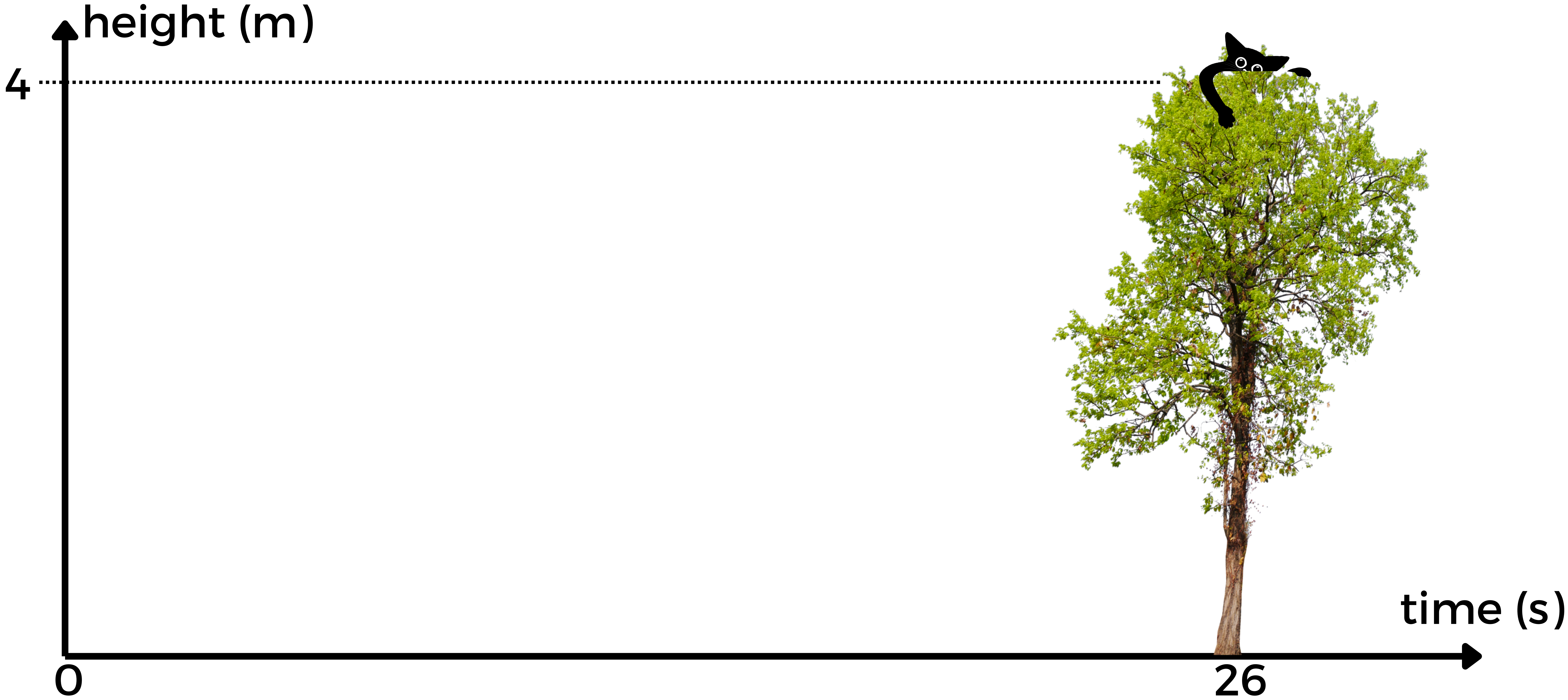
time (s)

0

Attosecond time resolution

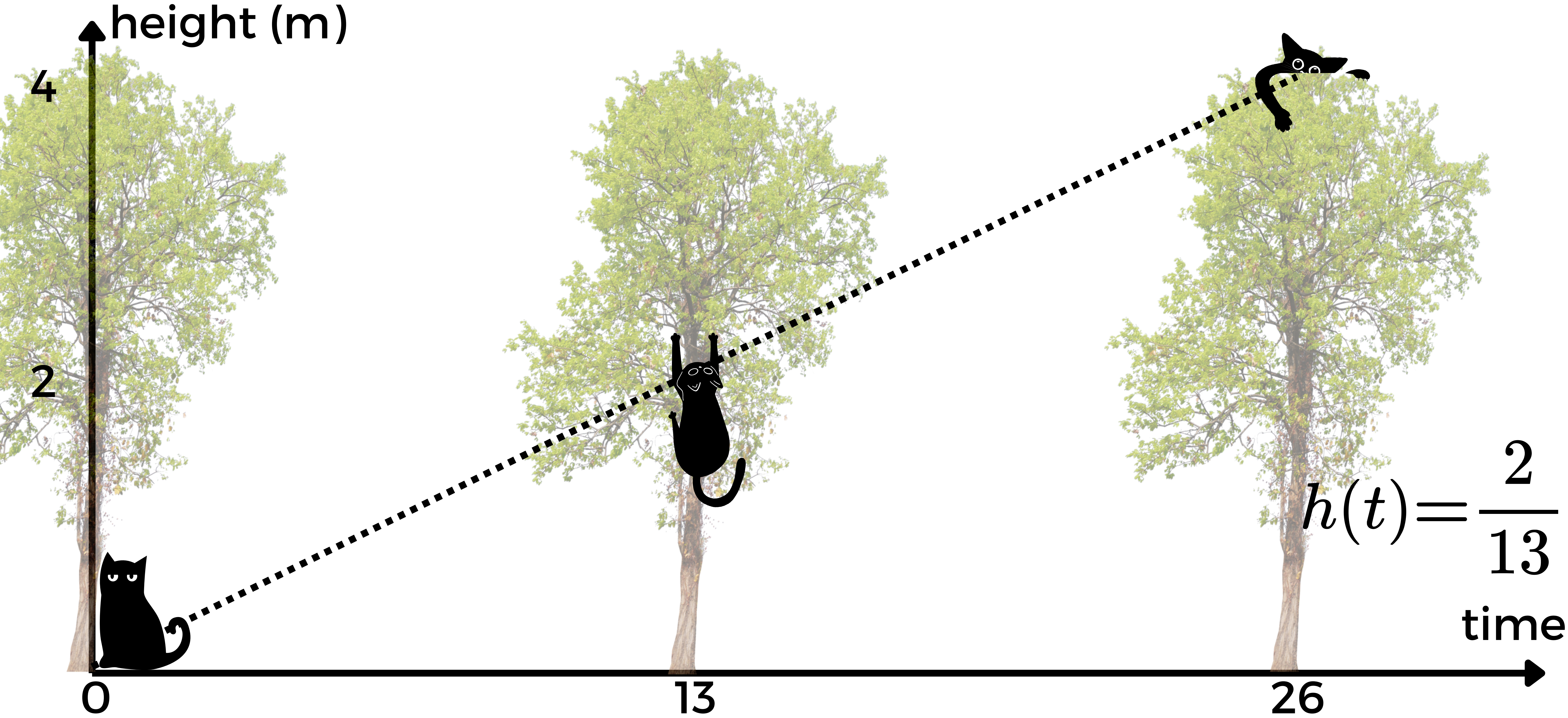


Attosecond time resolution

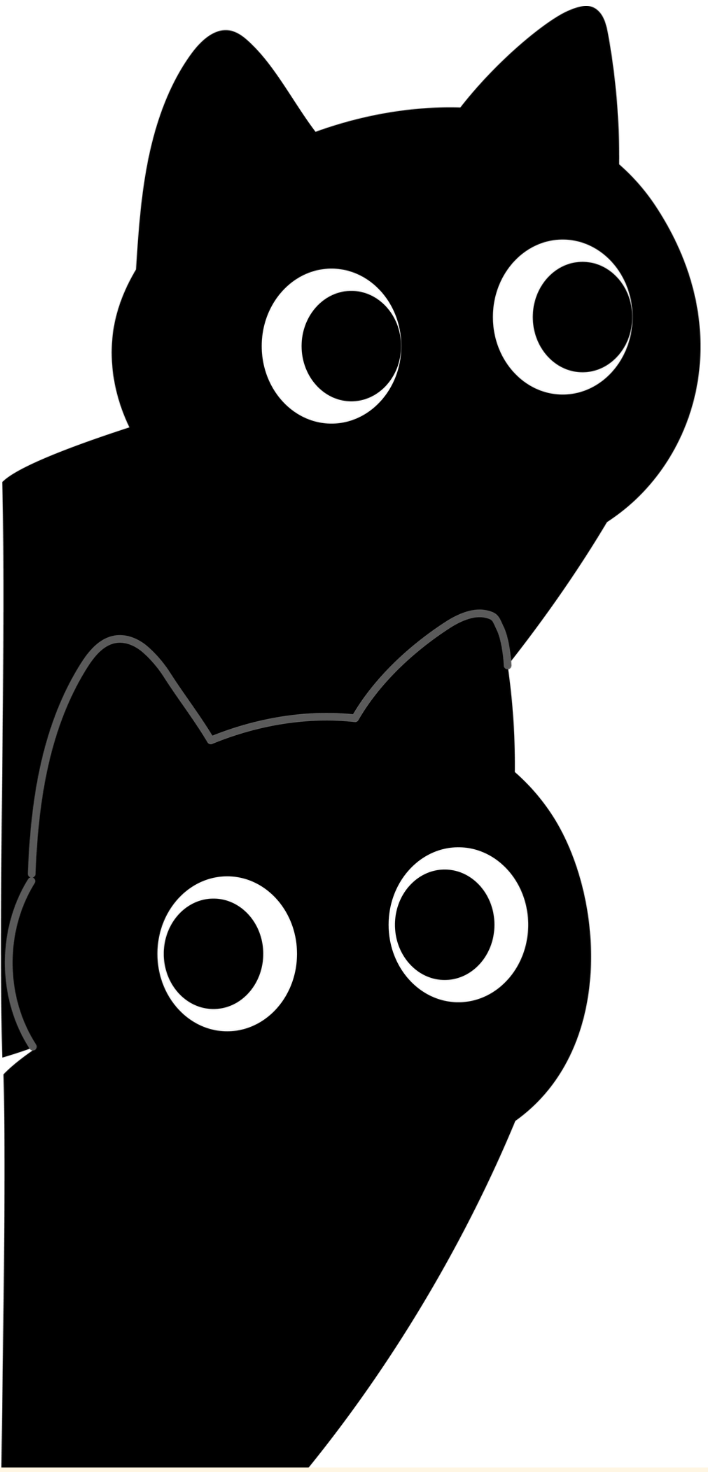


Attosecond time resolution

Attosecond time resolution

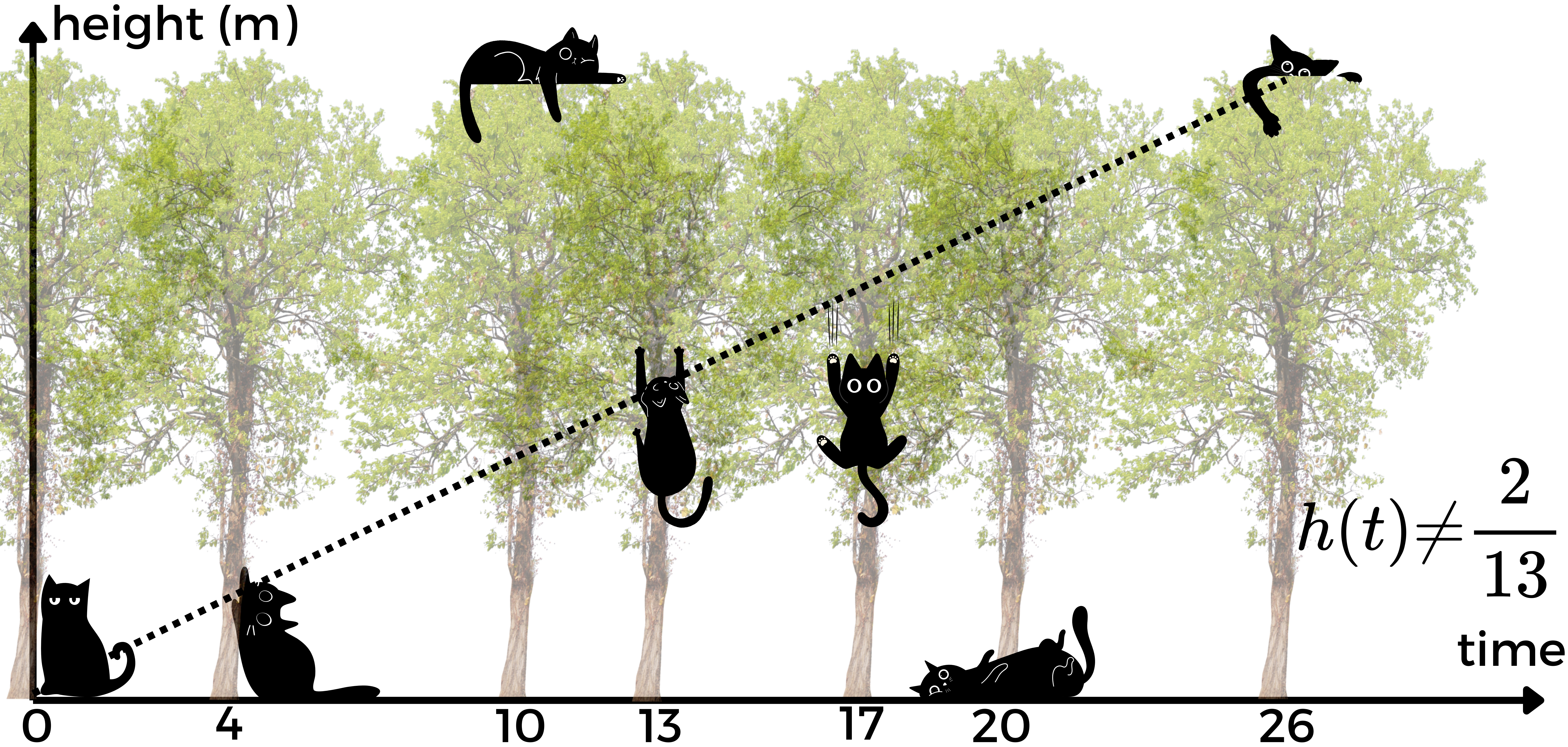


$$h(t) = \frac{2}{13} \cdot t$$



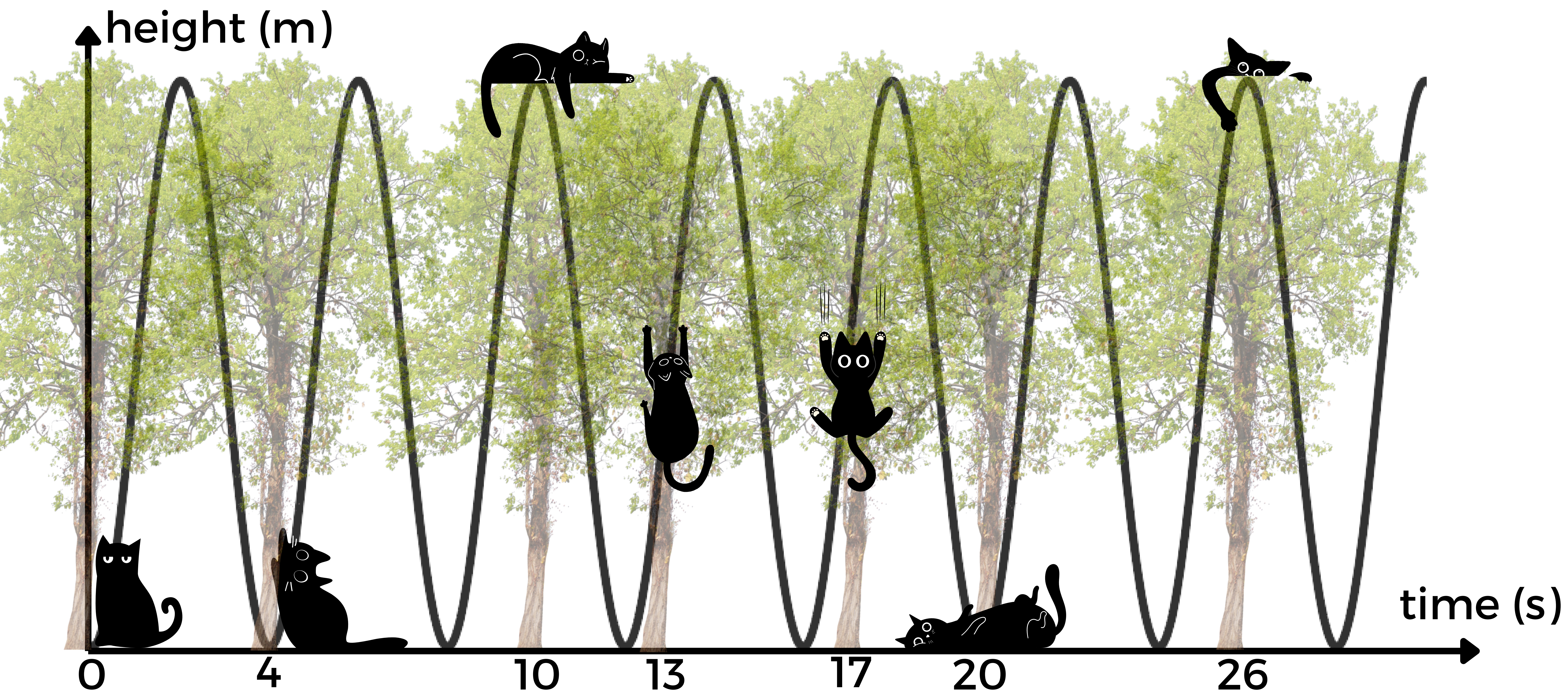
What would have happened
if we had taken more photos?

Attosecond time resolution



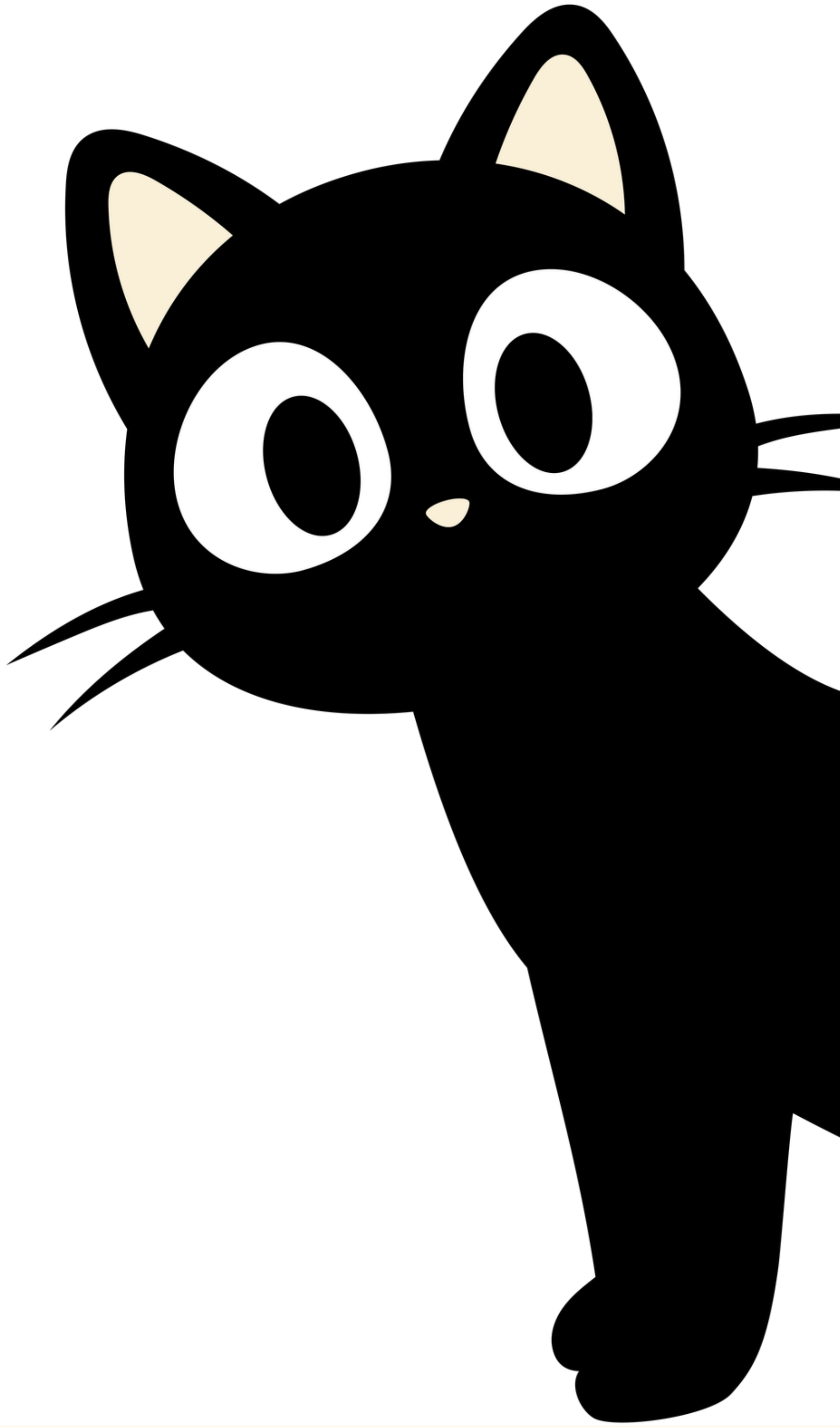
$$h(t) \neq \frac{2}{13} \cdot t$$

Attosecond time resolution

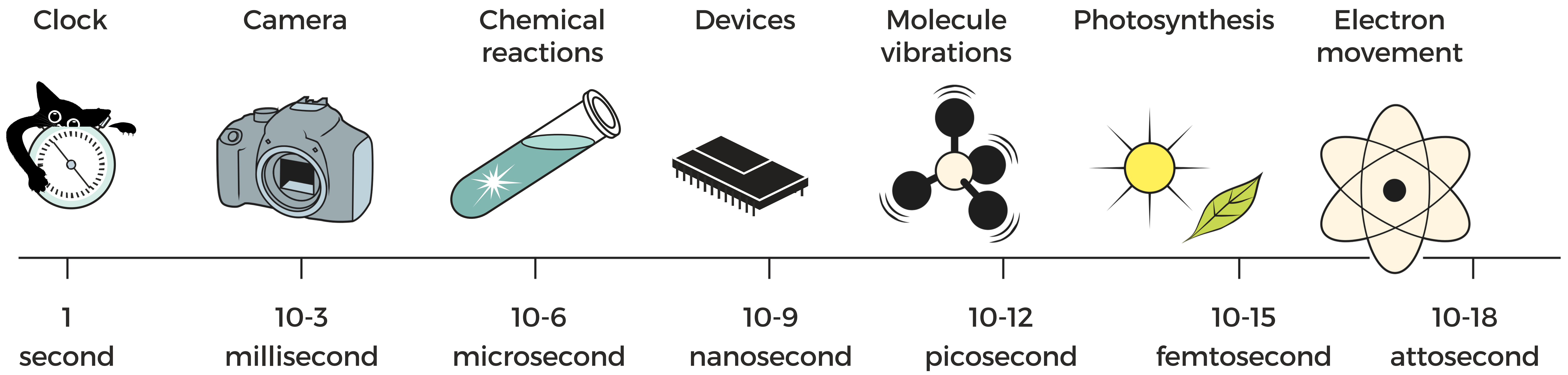


2h

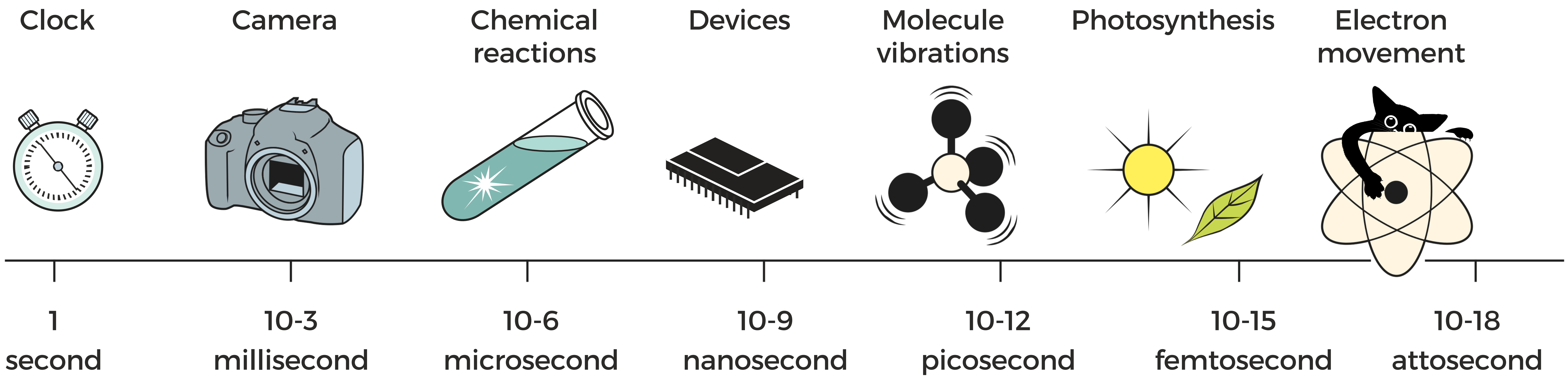
How to choose appropriate time resolution?



Attosecond time resolution

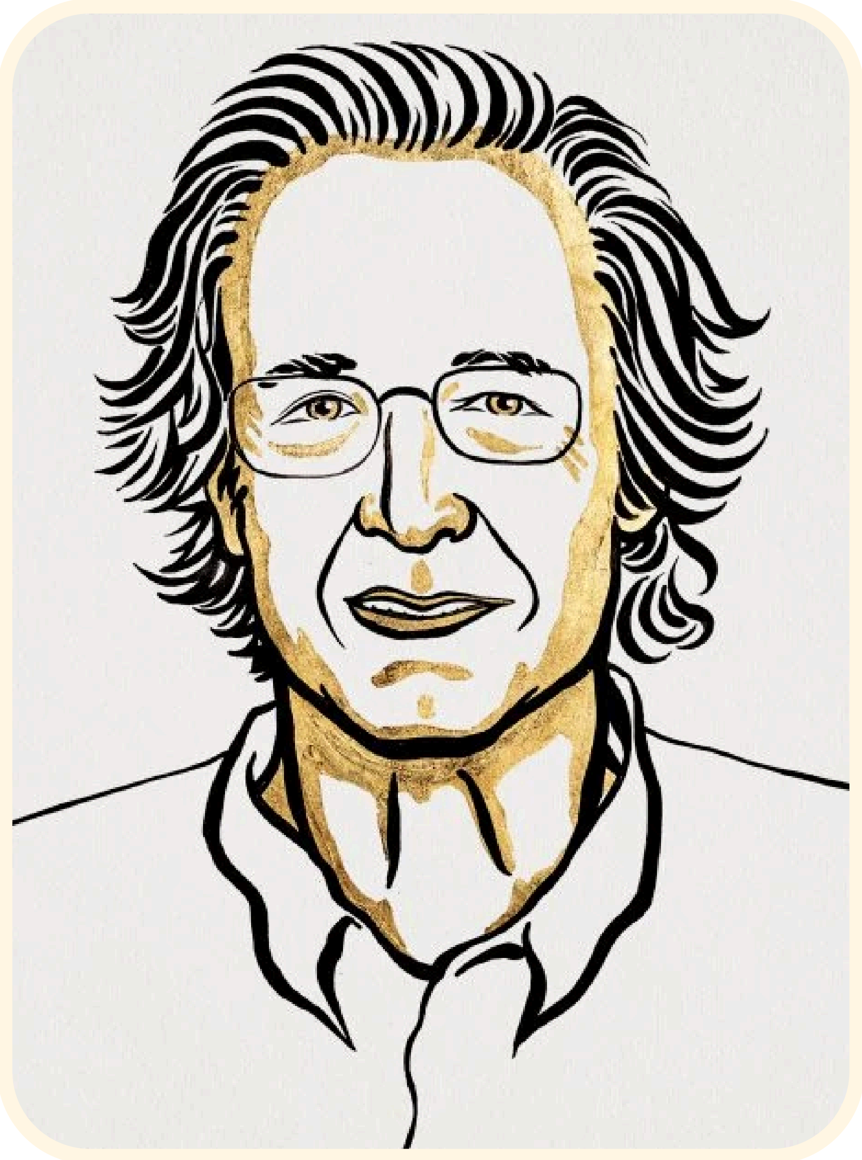


Attosecond time resolution



How to obtain attosecond time resolution?

Attosecond time resolution



Pierre Agostini

Ferenc Krausz

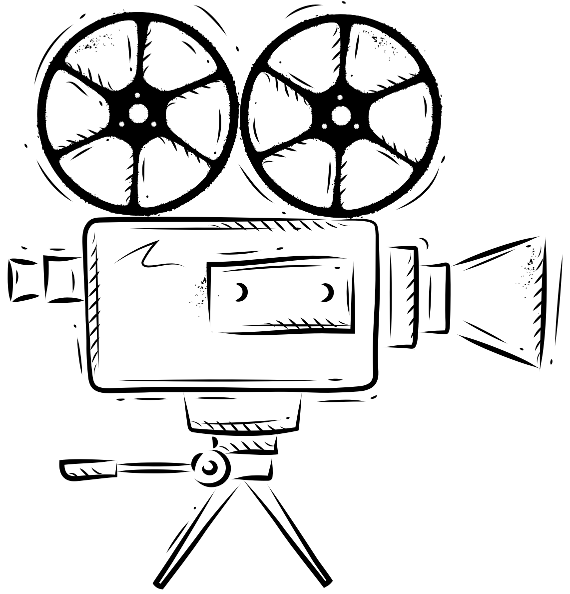
Anne L'Huillier

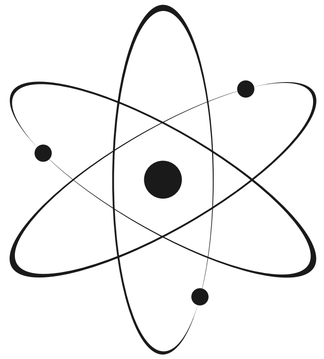
Nobel prize 2023

"For experimental methods that generate attosecond pulses of light for the study of electron dynamics in matter."

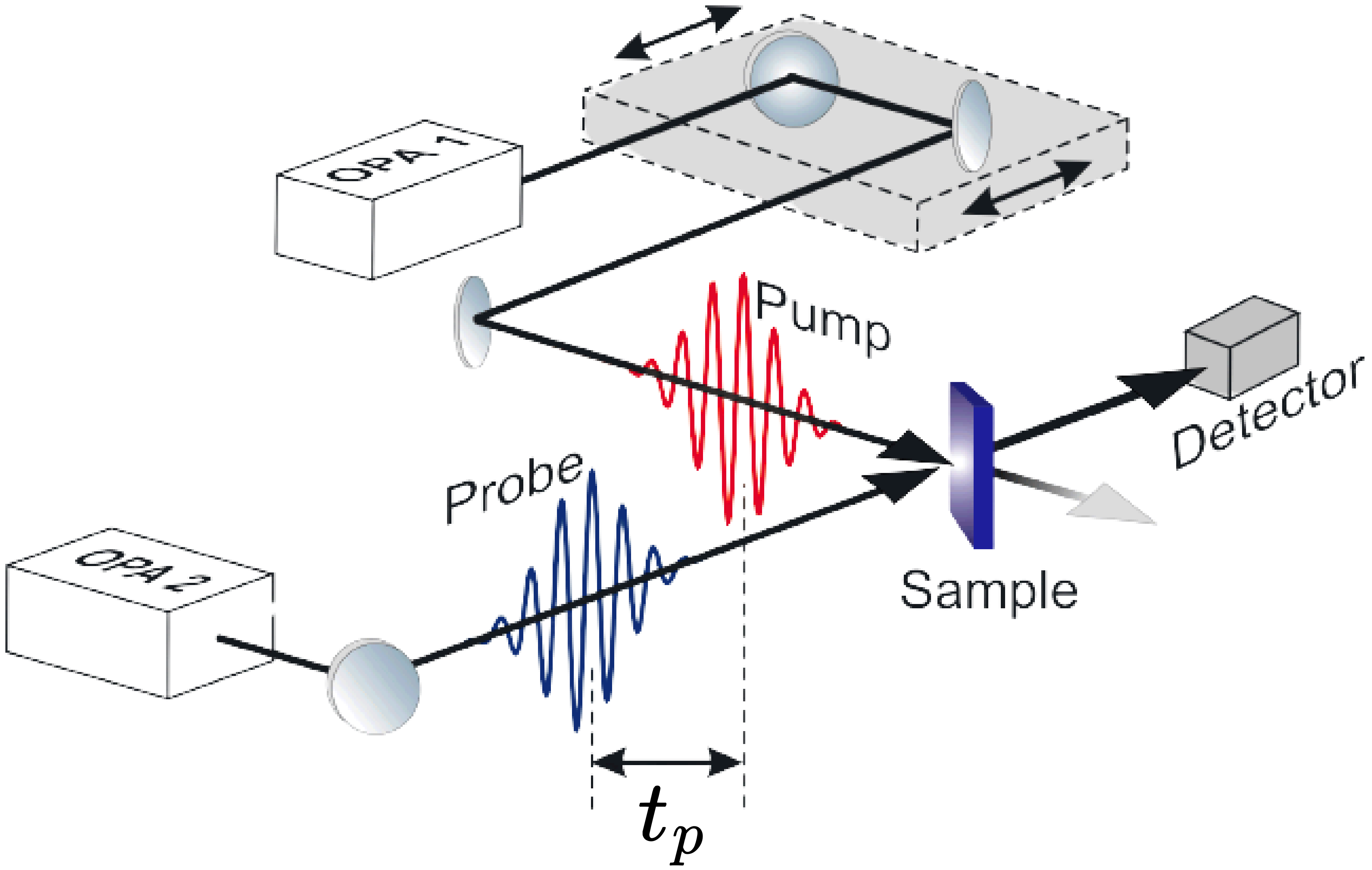
Attosecond time resolution

Filming of the electron motion





Pump-probe experiment



Attosecond pump-probe experiment

Letter | Published: 10 June 2010

Electron localization following attosecond molecular photoionization

G. Sansone, F. Kelkensberg, J. F. Pérez-Torres, F. Morales, M. F. Kling, W. Siu, O. Ghafur, P. Johnsson, M. Swoboda, E. Benedetti, F. Ferrari, F. Lépine, J. L. Sanz-Vicario, S. Zherebtsov, I. Znakovskaya, A. L'Huillier, M. Yu. Ivanov, M. Nisoli, F. Martín & M. J. J. Vrakking

Terawatt-attosecond hard X-ray free-electron laser at high repetition rate

Jiawei Yan, Weilun Qin, Ye Chen, Winfried Decking, Philipp Dijkstal, Marc Guetg, Ichiro Inoue, Naresh Kujala, Shan Liu, Tianyun Long, Najmeh Mirian & Gianluca Geloni

Nature Photonics **18**, 1293–1298 (2024) | Cite this article

Article | Published: 14 November 2010

High-energy isolated attosecond pulses generated by above-saturation few-cycle fields

F. Ferrari, F. Calegari, M. Lucchini, C. Vozzi, S. Stagira, G. Sansone & M. Nisoli

Tunable isolated attosecond X-ray pulses with gigawatt peak power from a free-electron laser

Joseph Duris, Siqi Li, Taran Driver, Elio G. Champenois, James P. MacArthur, Alberto A. Lutman, Zhen Zhang, Philipp Rosenberger, Jeff W. Aldrich, Ryan Coffee, Giacomo Coslovich, Franz-Josef Decker, James M. Glownia, Gregor Hartmann, Wolfram Helml, Andrei Kamalov, Jonas Knurr, Jacek Krzywinski, Ming-Fu Lin, Jon P. Marangos, Megan Nantel, Adi Natan, Jordan T. O'Neal, Niranjan Shivaram, Peter Walter, Anna Li Wang, James J. Welch, Thomas J. A. Wolf, Joseph Z. Xu, Matthias F. Kling, Philip H. Bucksbaum, Alexander Zholents, Zhirong Huang, James P. Cryan & Agostino Marinelli — Show fewer authors

Nature Photonics **14**, 30–36 (2020) | Cite this article

Isolated Single-Cycle Attosecond Pulses

G. SANSONE, E. BENEDETTI, F. CALEGARI, C. VOZZI, L. AVALDI, R. FLAMMINI, L. POLETTO, P. VILLORESI, C. ALTUCCI, R. VELOTTA, S. STAGIRA, S. DE SILVESTRI, AND M. NISOLI fewer Authors Info & Affiliations

SCIENCE • 20 Oct 2006 • Vol 314, Issue 5798 • pp. 443-446 • DOI: 10.1126/science.1132838

Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses

F. CALEGARI, D. AYUSO, A. TRABATTONI, L. BELSHAW, S. DE CAMILLIS, S. ANUMULA, F. FRASSETTO, L. POLETTO, A. PALACIOS, P. DECLEVA, J. B. GREENWOOD, F. MARTÍN, AND M. NISOLI fewer Authors Info & Affiliations

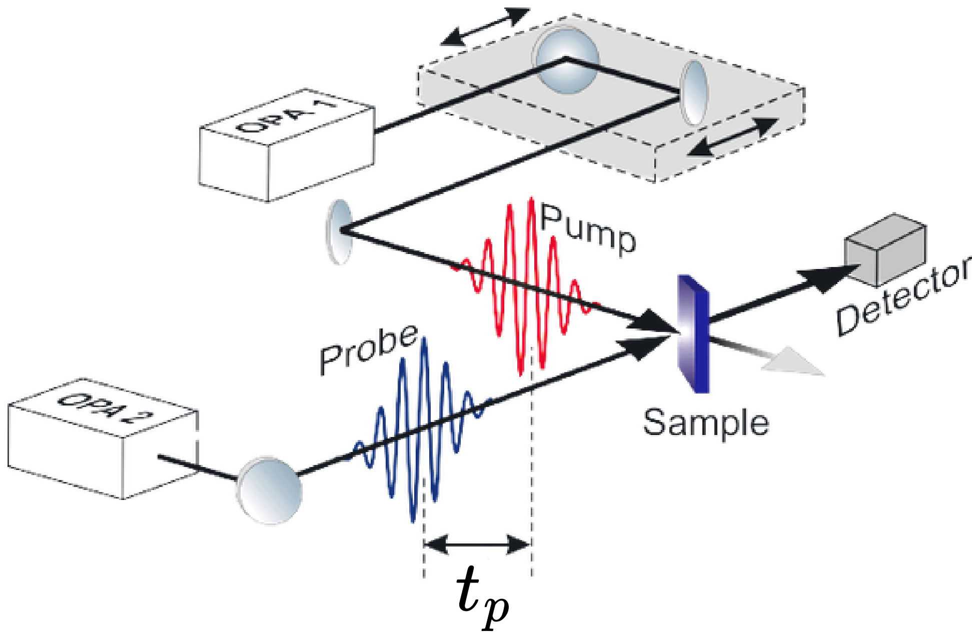
SCIENCE • 17 Oct 2014 • Vol 346, Issue 6207 • pp. 336-339 • DOI: 10.1126/science.1254061

Coherent sub-femtosecond soft x-ray free-electron laser pulses with nonlinear compression

Eduard Prat; Alexander Malyzhenkov; Christopher Arrell; Paolo Craievich; Sven Reiche; Thomas Schietinger; Guanglei Wang

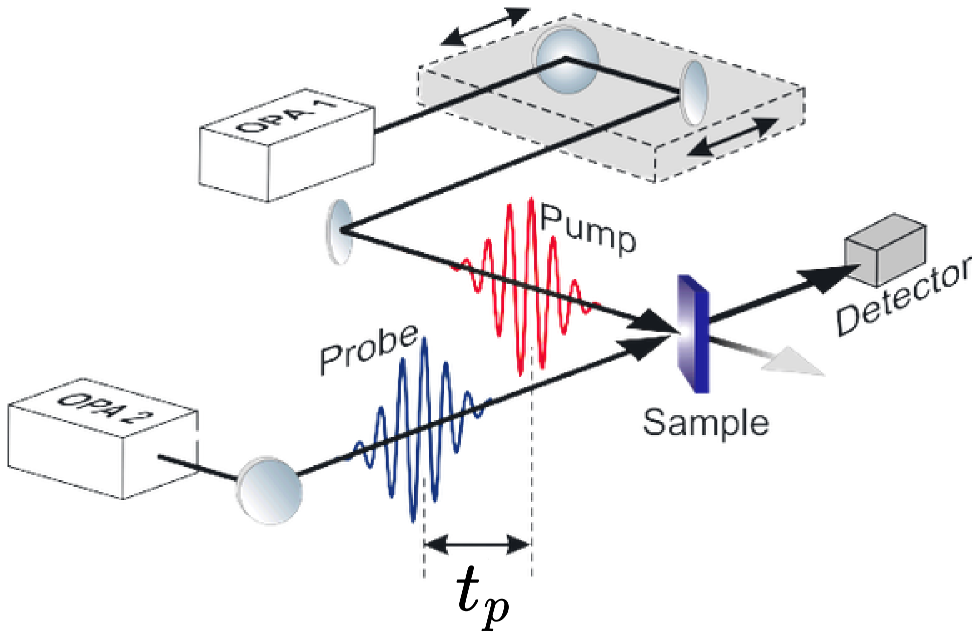
Attosecond pump-probe experiment

pump - probe experiment

pump	probe	experiment
x-ray / UV	x-ray / UV	
linear / circular	linear / circular	
excitation / ionization	absorption photoemission scattering (resonant / nonresonant)	gas phase solid state films liquid

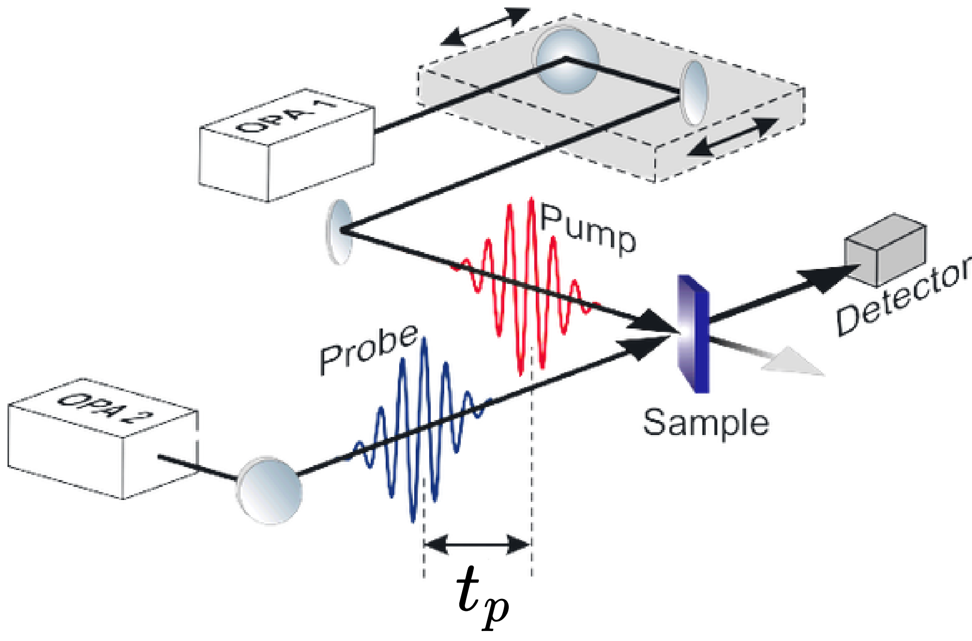
Attosecond pump-probe experiment

pump	-	probe	experiment
x-ray / UV		x-ray / UV	
linear / circular		linear / circular	
excitation / ionization		absorption photoemission scattering (resonant / nonresonant)	gas phase solid state films liquid

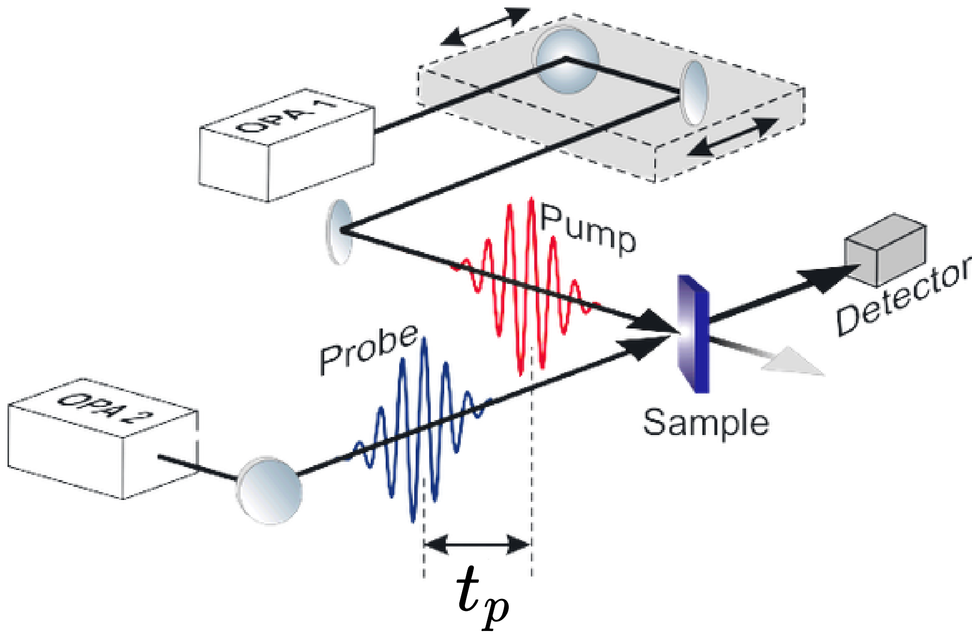


Attosecond pump-probe experiment

pump	-	probe	experiment
x-ray / UV		x-ray / UV	
linear / circular		linear / circular	
excitation / ionization		absorption photoemission scattering (resonant / nonresonant)	gas phase solid state films liquid

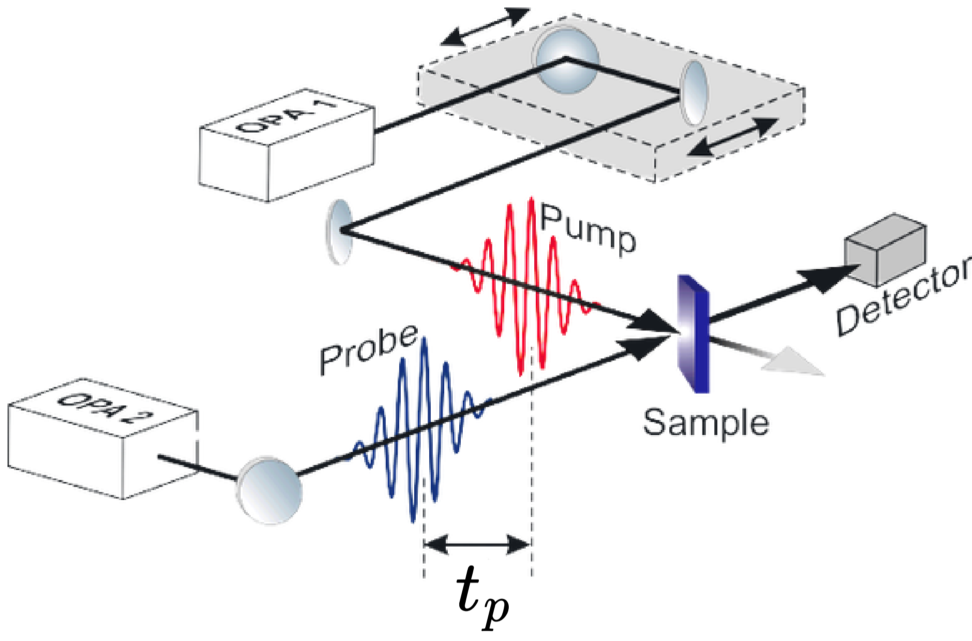


Attosecond pump-probe experiment

pump	-	probe	experiment
x-ray / UV		x-ray / UV	
linear / circular		linear / circular	
excitation / ionization		absorption photoemission scattering (resonant / nonresonant)	gas phase solid state films liquid

© picture from G. Cerullo et. al., 2006, “Time-resolved methods in biophysics.”

Attosecond pump-probe experiment

pump	-	probe	experiment
UV		x-ray	
linear		linear	
neutral excitation		resonant scattering	aligned molecules (gas phase / films)

Attosecond imaging experiments have already been conducted on LCLS

Non-linear enhancement of ultrafast X-ray diffraction through transient resonances

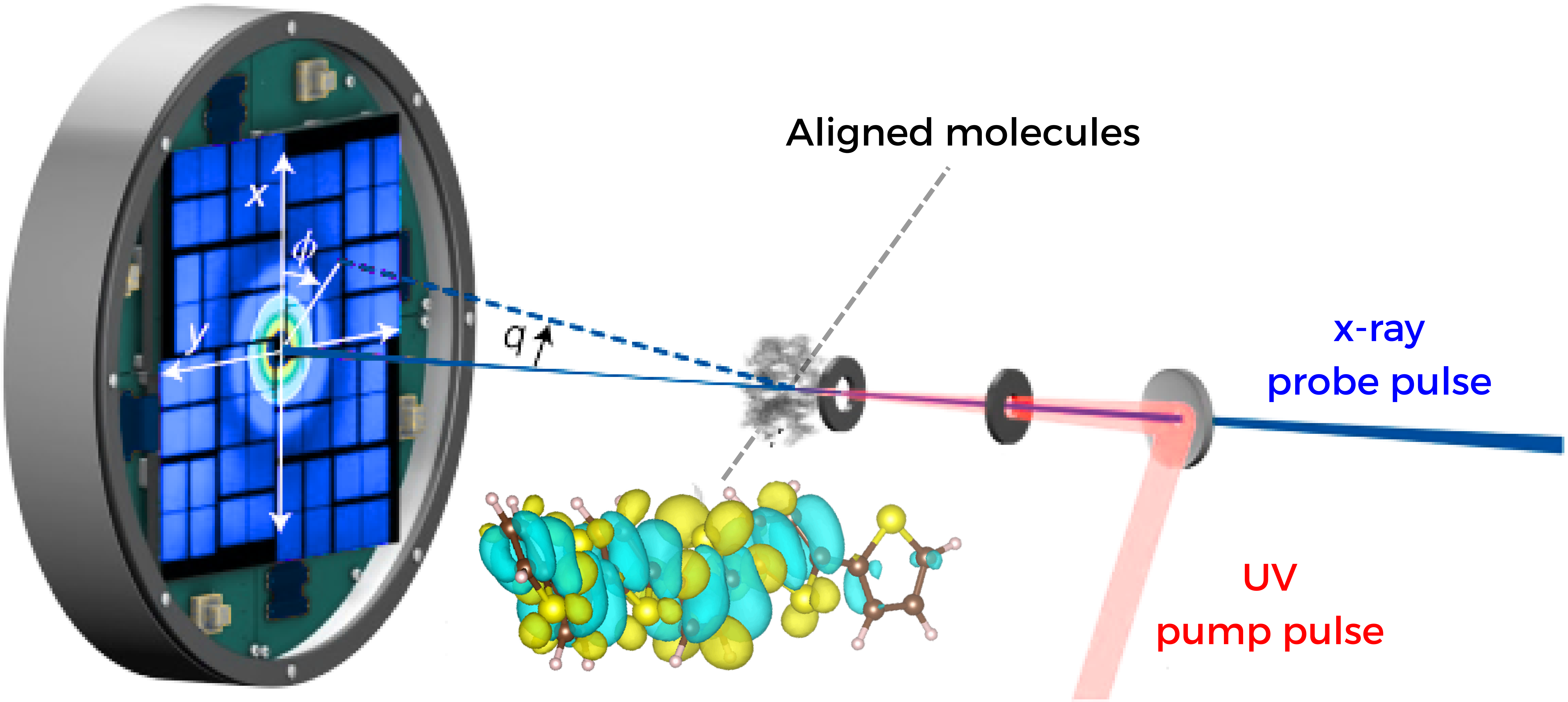
Stephan Kuschel, Phay J. Ho, Andre Al Haddad, Felix F. Zimmermann, Leonie Flueckiger, Matthew R. Ware, Joseph Duris, James P. MacArthur, Alberto Lutman, Ming-Fu Lin, Xiang Li, Kazutaka Nakahara, Jeff W. Aldrich, Peter Walter, Linda Young, Christoph Bostedt, Agostino Marinelli & Tais Gorkhover

Nature Communications **16**, Article number: 847 (2025) | Cite this article

Nonlinear reversal of photo-excitation on the attosecond time scale improves ultrafast x-ray diffraction images

Anatoli Ulmer,[1,*] Phay J. Ho,[2] Bruno Langbehn,[3] Stephan Kuschel,[1,4] Linos Hecht,[5] Razib Obaid,[6] Simon Dold,[7] Taran Driver,[6,8] Joseph Duris,[6] Ming-Fu Lin,[6] David Cesar,[6] Paris Franz,[6] Zhaoheng Guo,[6,9] Philip A. Hart,[6] Andrei Kamalov,[6] Kirk A. Larsen,[6] Xiang Li,[6] Michael Meyer,[7] Kazutaka Nakahara,[6] Robert G. Radloff,[1] River Robles,[6] Lara Rönnebeck,[1] Nick Sudar,[6] Adam M. Summers,[6] Linda Young,[2] Peter Walter,[6] James Cryan,[6,8] Christoph Bostedt,[10,11] Daniela Rupp,[5] Agostino Marinelli,[6] and Tais Gorkhover[1,†]

Attosecond momentum-resolved pump-probe experiment



Sexithiophene

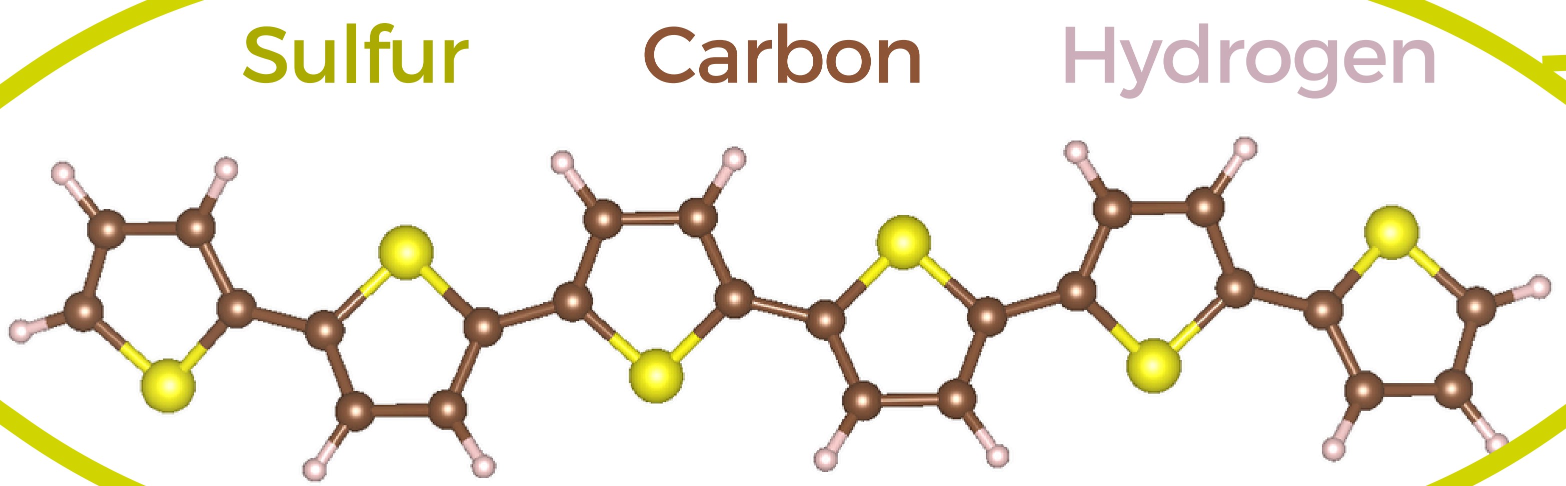
multiple heavy atoms

optoelectronic applications

Solid-State Conformation, Molecular Packing, and Electrical and Optical Properties of Processable β-Methylated Sexithiophenes

Giovanna Barbarella,[*,†] Massimo Zambianchi,[†] Luciano Antolini,[‡] Paolo Ostoja,[§] Piera Maccagnani,[§] Alessandro Bongini,[‖] Elisabeth A. Marseglia,[⊥] Emilio Tedesco,[⊥] ...ppe Gigli,[#] and Roberto Cingolani[#]

stable



OFETs

Electronic transport in field-effect transistors of sexithiophene

P. Stallinga and H. L. Gomes
Universidade do Algarve, Faculdade de Ciências e Tecnologia, Campus de Gambelas, P-8000 Faro, Portugal

F. Biscarini and M. Murgia
CNR-Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Via P. Gobetti 101, I-40129 Bologna, Italy

D. M. de Leeuw
Philips Research, Prof. Holstlaan 4, NL-5656 AA Eindhoven, The Netherlands

(Received 4 February 2004; accepted 14 July 2004)

tunable by adding functional groups

Tuning the Semiconducting Properties of Sexithiophene by α,ω-Substitution—α,ω-Diperfluorohexylsexithiophene: The First n-Type Sexithiophene for Thin-Film Transistors**

Antonio Facchetti, Yvonne Deng, Anchuan Wang, Yoshihiro Koide, Henning Sirringhaus, Tobin J. Marks,* and Richard H. Friend*

charge mobility

Polymorphism and Charge Transport in Vacuum-Evaporated Sexithiophene Films

B. Servet,[†] G. Horowitz,[‡] S. Ries,[†] O. Lagorsse,[†] P. Alnot,[†,*] A. Yassar,[‡] F. Deloffre,[‡] P. Srivastava,[‡] R. Hajlaoui,[‡] P. Lang,[‡] and F. Garnier[‡]

Thomson CSF/LCR, Domaine de Corbeville, 91404 ORSAY CEDEX, France, and Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry-Dunant, 94320 Thiais, France

Received April 7, 1994. Revised Manuscript Received June 29, 1994[®]

luminescence quencher

Synthesis and properties of end-capped sexithiophenes incorporating the ethylene dithiothiophene unit

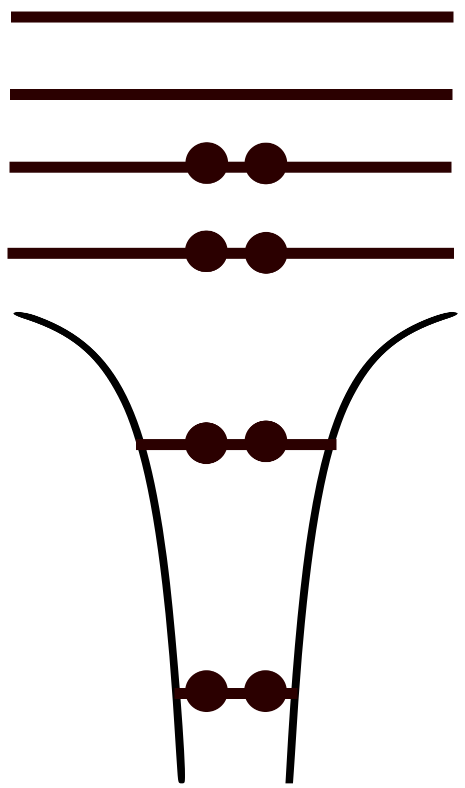
Christopher R. Mason,[a] Peter J. Skabara,[*a] Domenico Cupertino,[b] John Schofield,[b] Farideh Meghdadi,[c] Berndt Ebner[c] and N. Serdar Sariciftci[c]

Received 8th October 2004, Accepted 21st December 2004
First published as an Advance Article on the web 2nd February 2005
DOI: 10.1039/b415610b

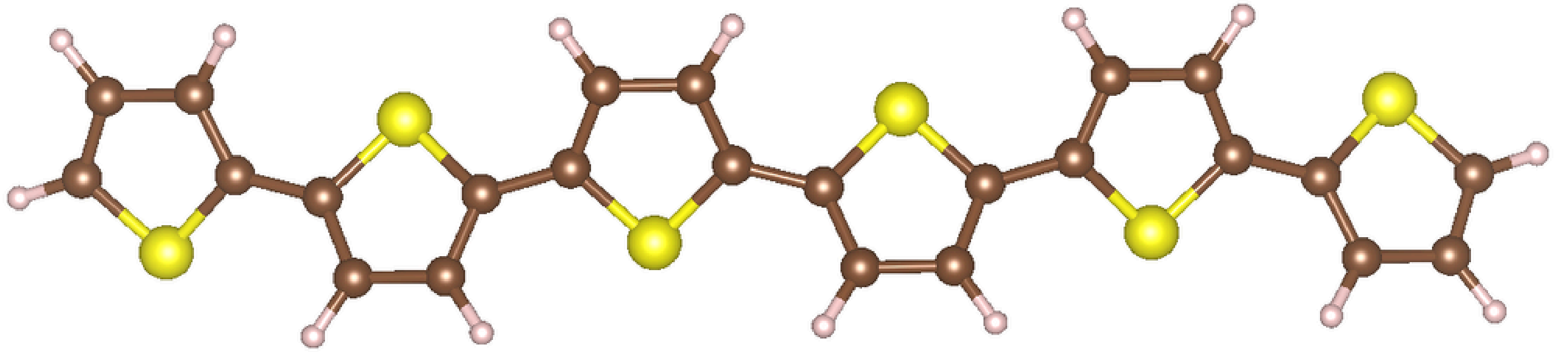
How do we describe this experiment?

Attosecond momentum-resolved RIXS

At the beginning we have a single closed-shell molecule in the ground state.

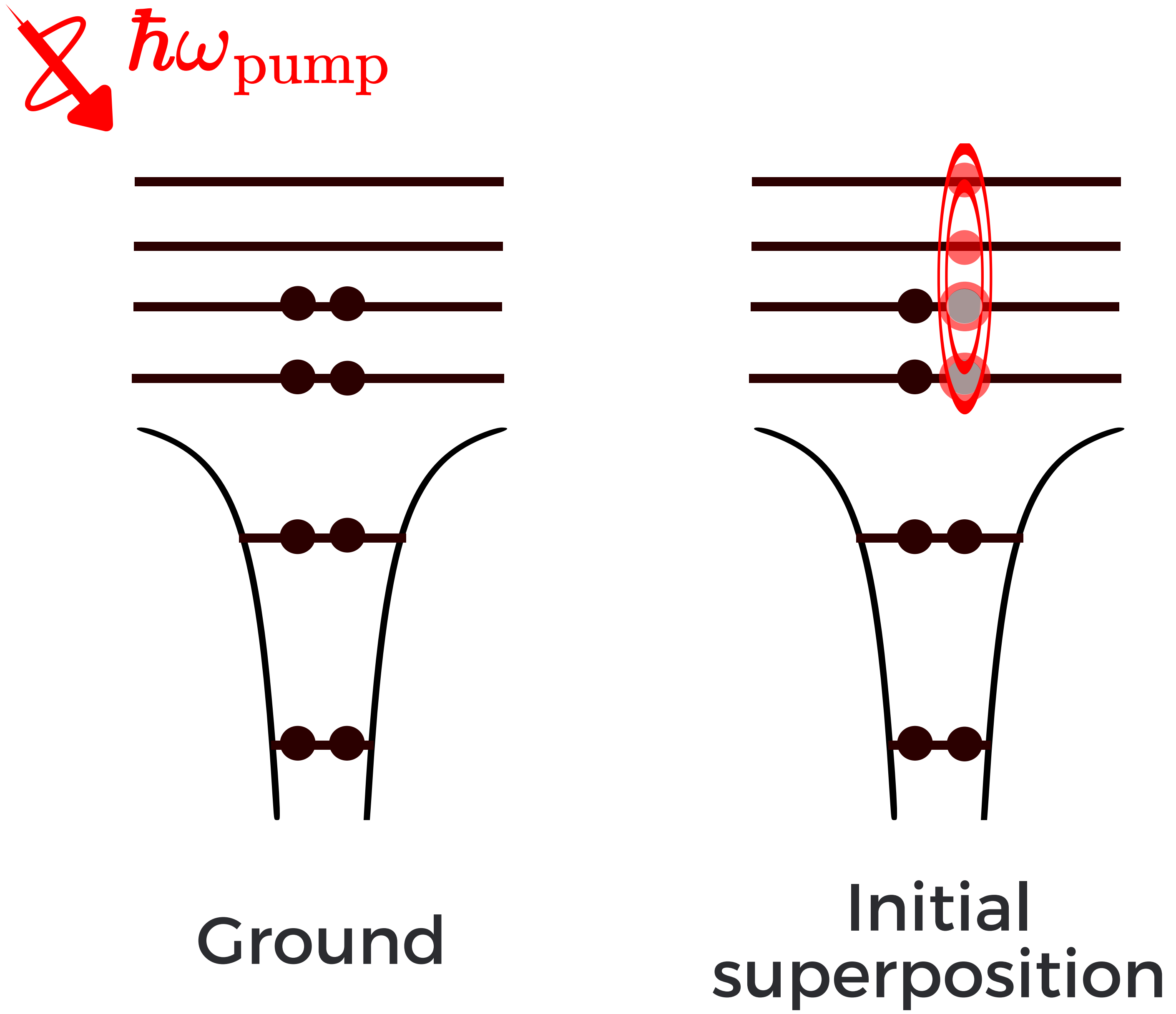


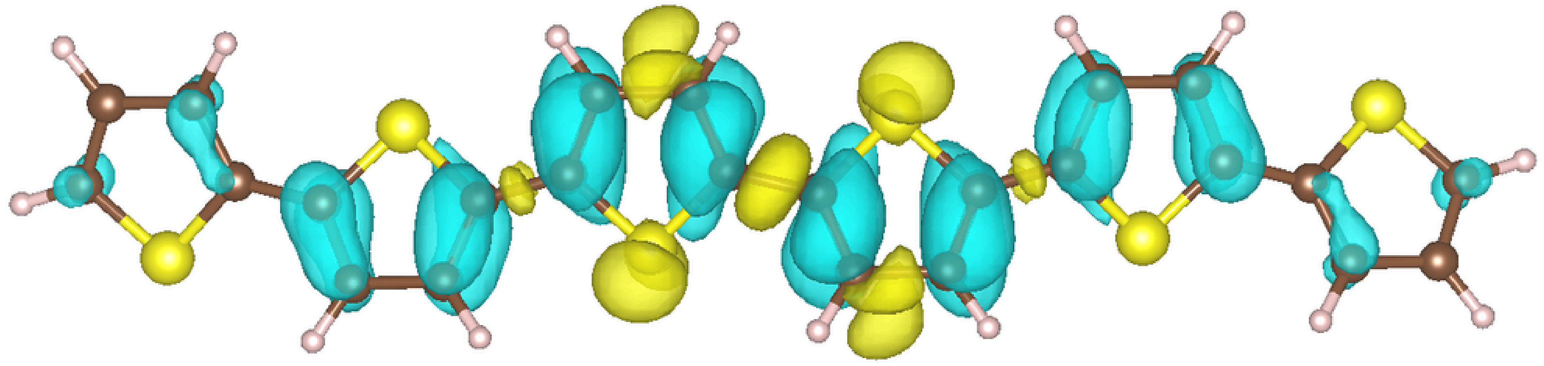
Ground



Attosecond momentum-resolved RIXS

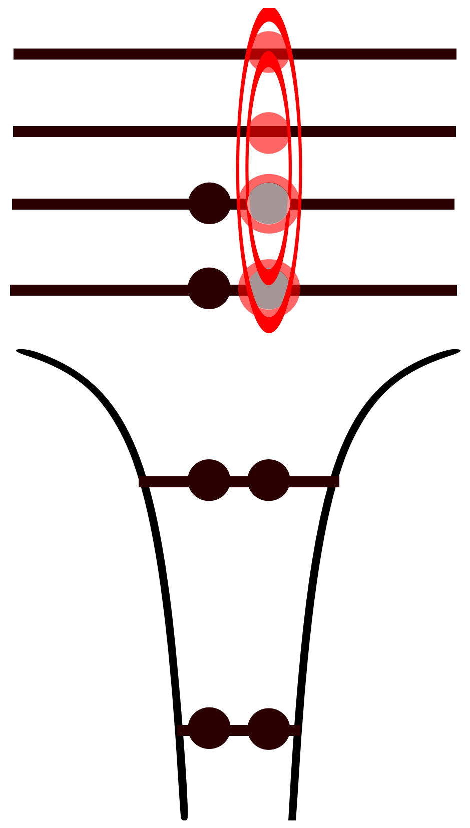
UV pump pulse excites electrons from HOMOs orbitals to LUMOs orbitals and creates a superposition of states (initial state).





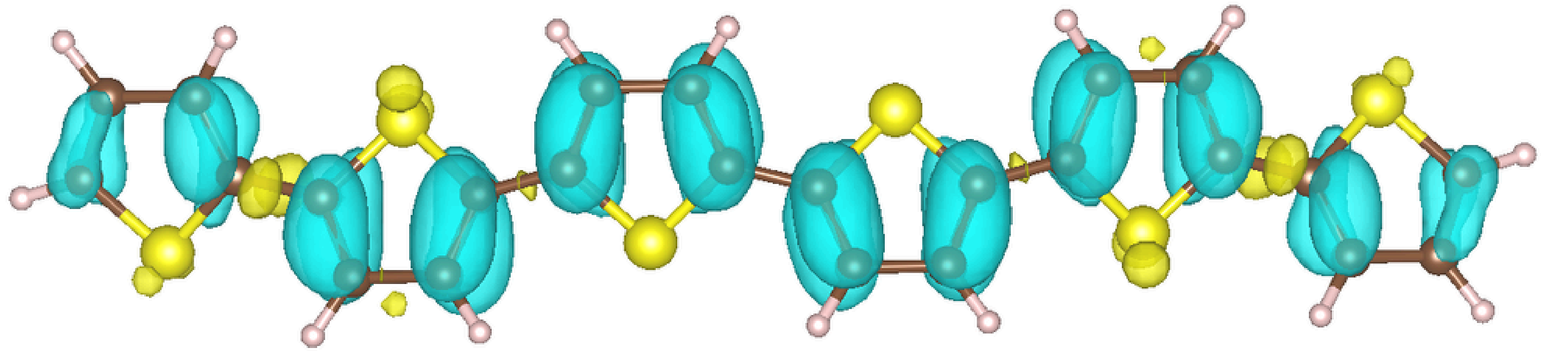
Attosecond momentum-resolved RIXS

This initial state evolves in time.

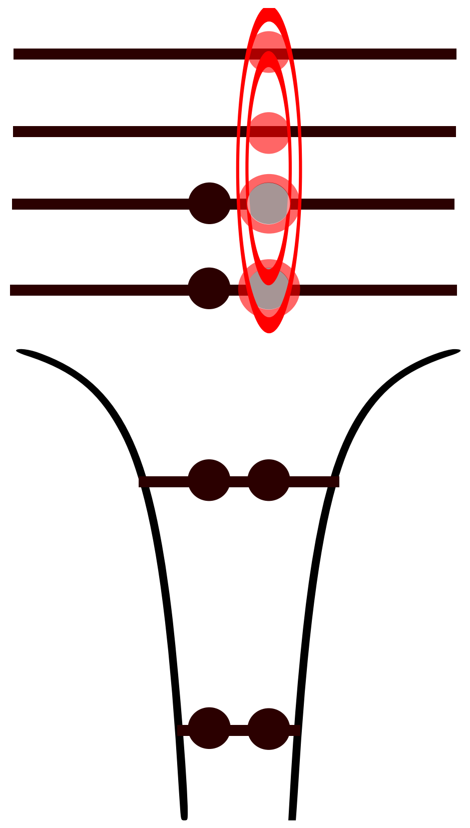


Initial superposition

$t_p = 1 \text{ fs}$

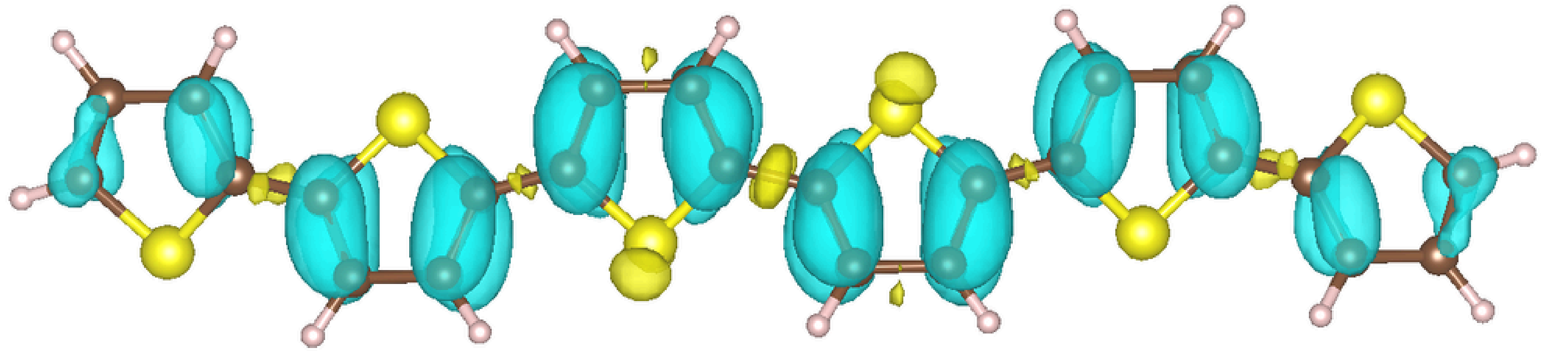


This initial state evolves in time.



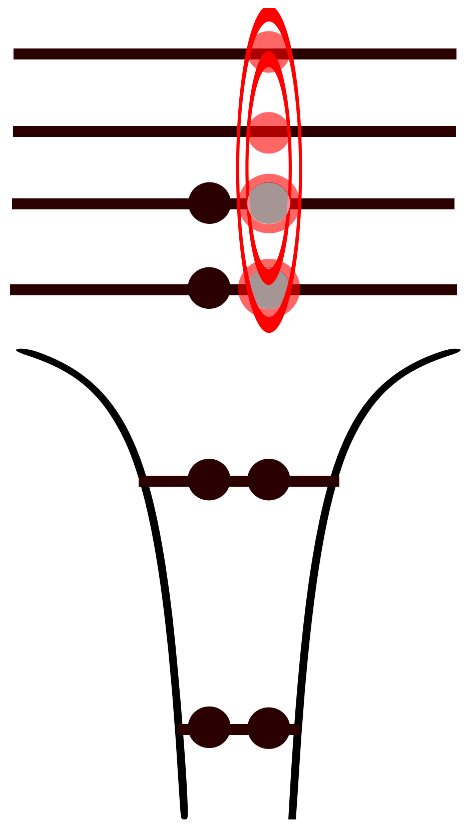
Initial
superposition

$t_p = 2$ fs



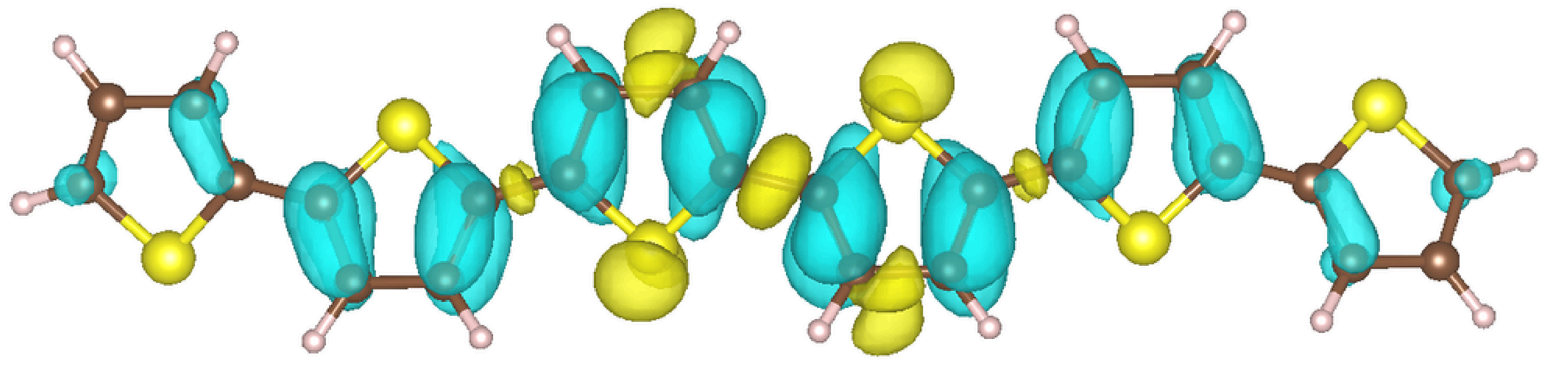
Attosecond momentum-resolved RIXS

This initial state evolves in time.



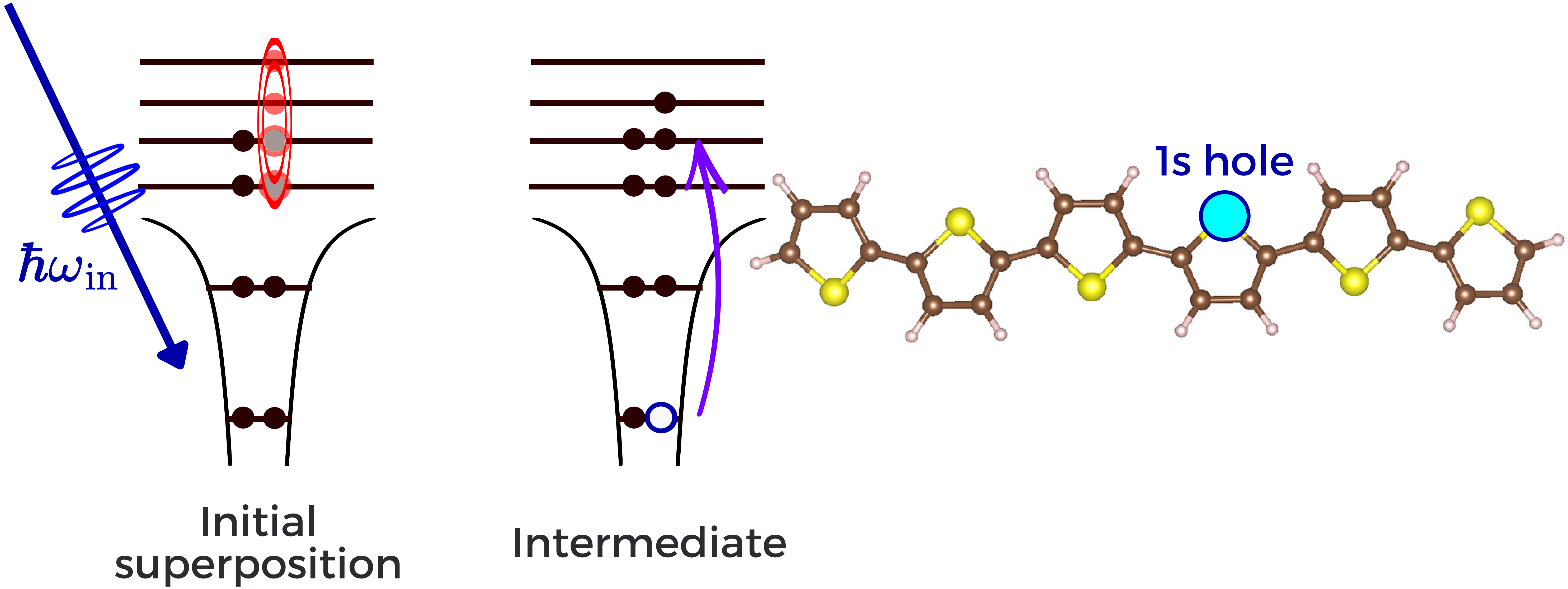
Initial superposition

$t_p = 3$ fs



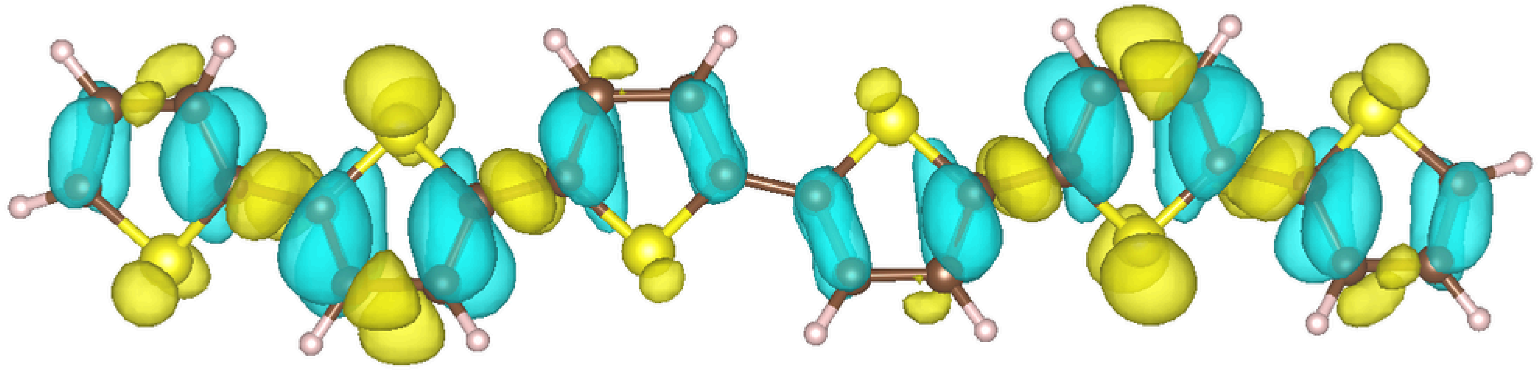
Attosecond momentum-resolved RIXS

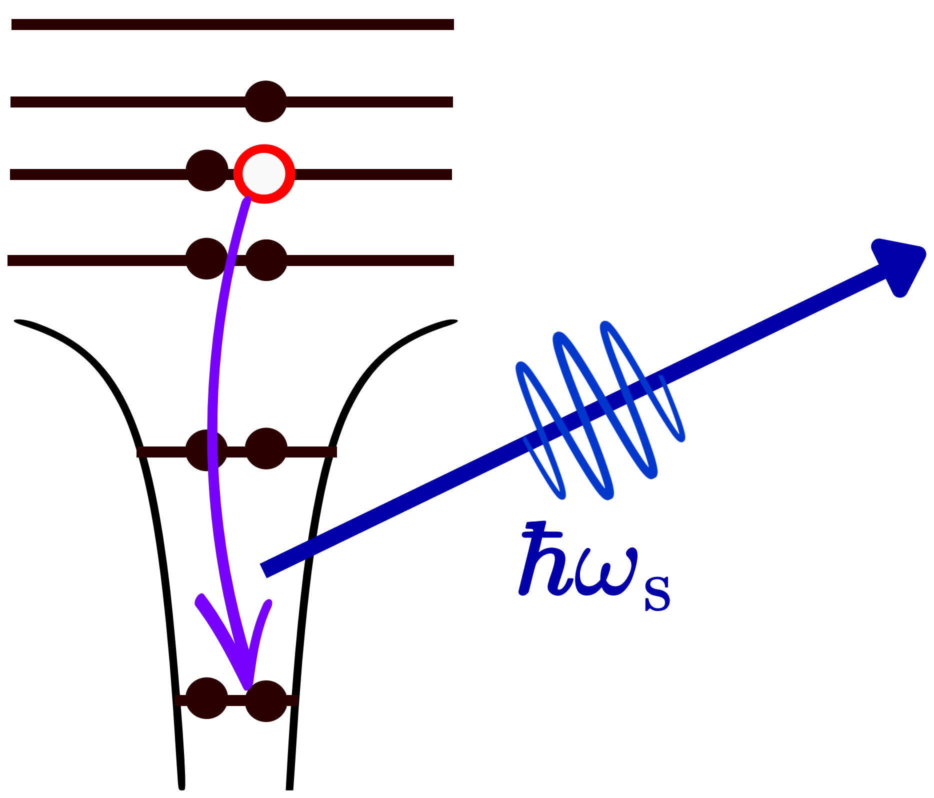
X-ray probe pulse is resonant to the K-edge of the atom chosen.
It puts the molecule into one of the intermediate states.



Attosecond momentum-resolved RIXS

Intermediate state relaxation moves the molecule to one of the final states and creates the photon with energy in X-ray region.

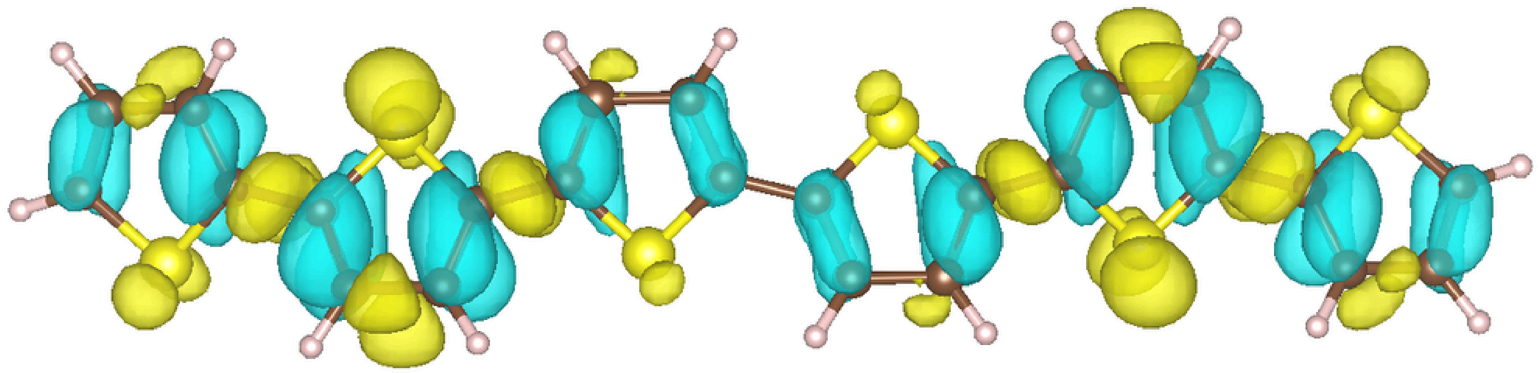


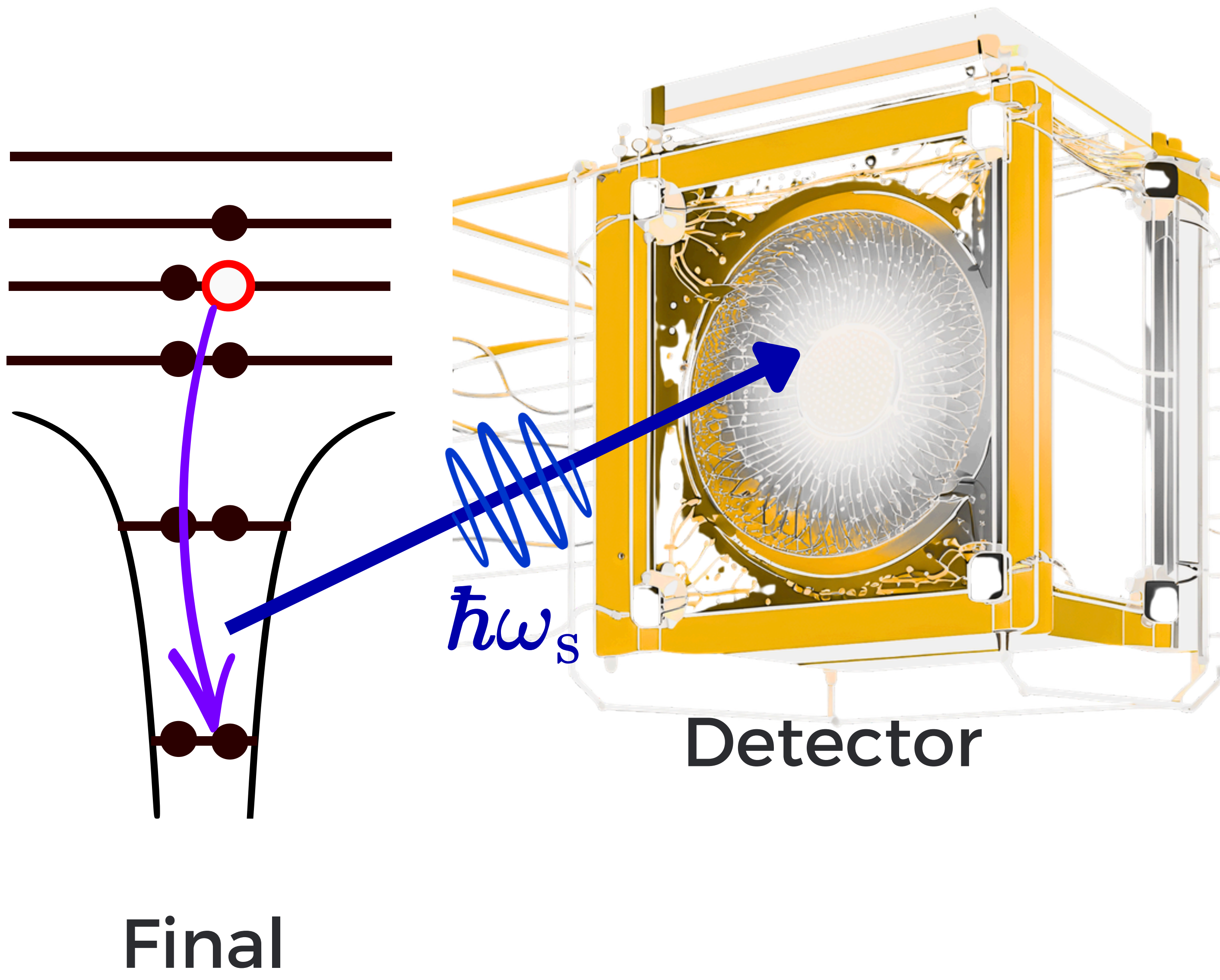


Final

Attosecond momentum-resolved RIXS

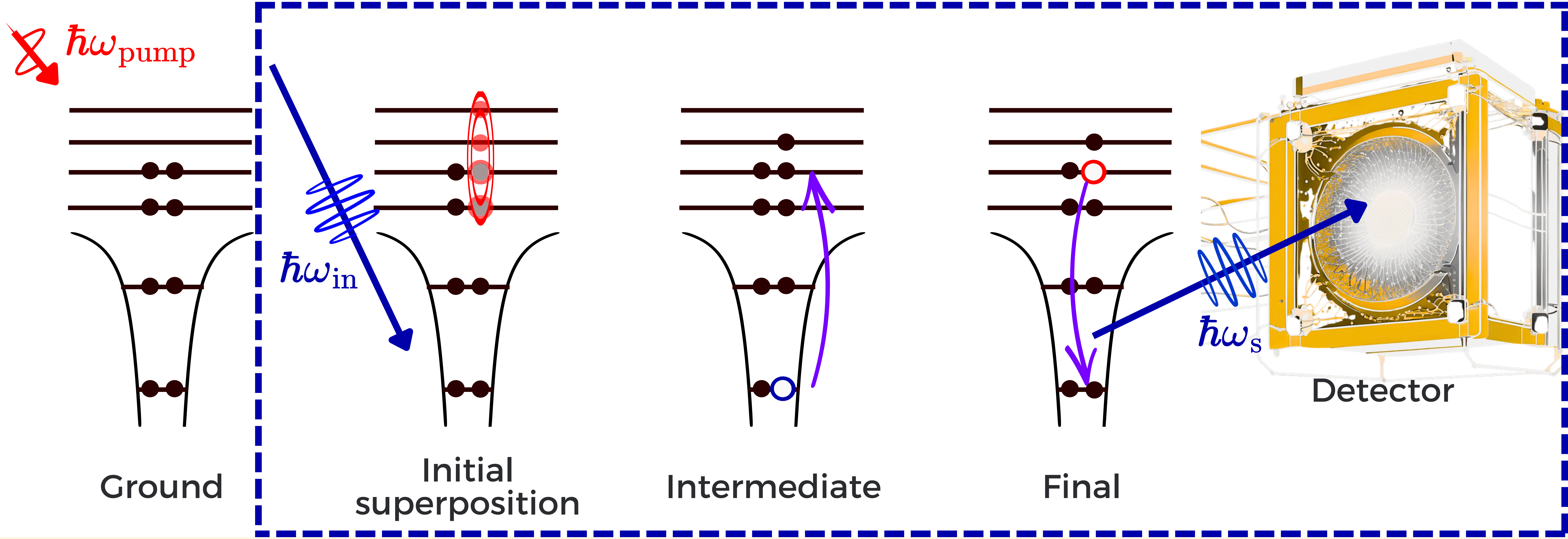
The momentum of the photon emitted is detected with a momentum-resolved detector.





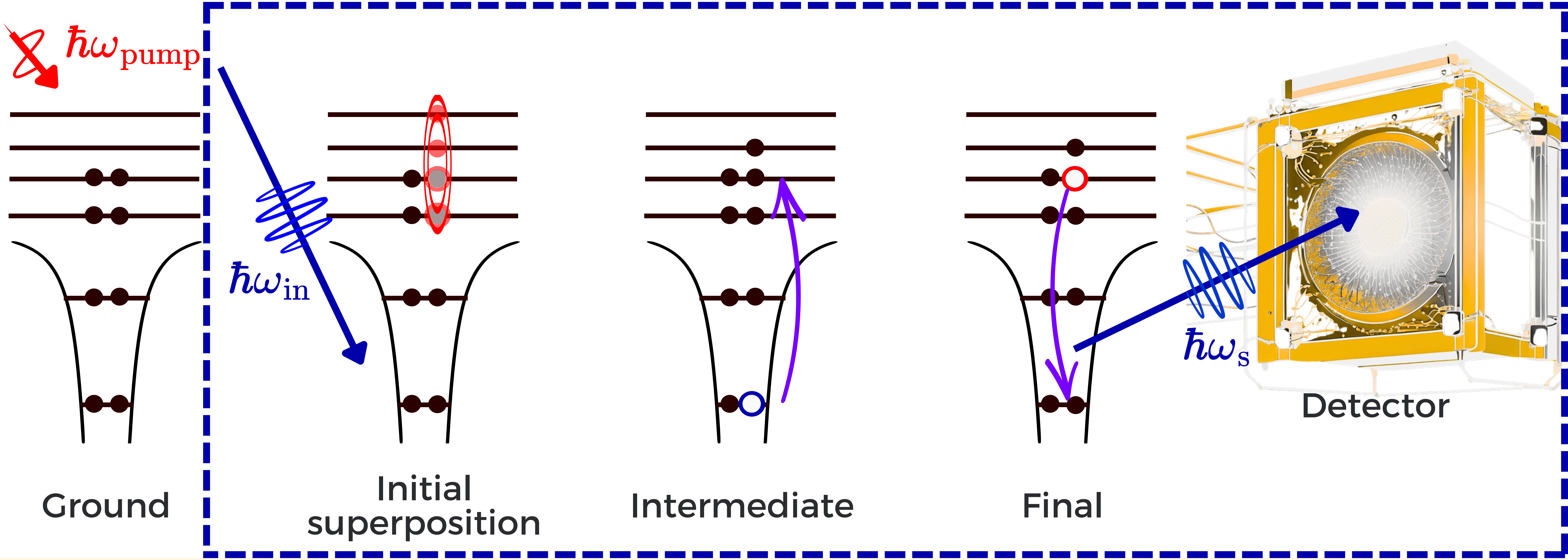
Attosecond momentum-resolved RIXS

Spatial and temporal resolutions are achieved because the probe pulse is in X-ray region.



Attosecond momentum-resolved RIXS

$$P(\mathbf{Q},t_p) \sim \sum_F \left| \sum_J e^{i\mathbf{Q}\cdot\mathbf{R}_J} \cdot \frac{\langle \Psi_F | \boldsymbol{\epsilon}_\mathrm{s}^* \cdot \boldsymbol{\nabla} | \Psi_J \rangle \langle \Psi_J | \boldsymbol{\epsilon}_\mathrm{in} \cdot \boldsymbol{\nabla} | \sum_n C_n e^{-i\varepsilon_n t_p} \Psi_n \rangle}{\left(\omega_\mathrm{s} + \varepsilon_F - \varepsilon_J + i\frac{\Gamma}{2}\right)} \cdot e^{-\frac{(\varepsilon_F + \omega_\mathrm{s} - \varepsilon_n - \omega_\mathrm{in})^2 \tau_p^2}{8\ln 2}} \right|^2$$

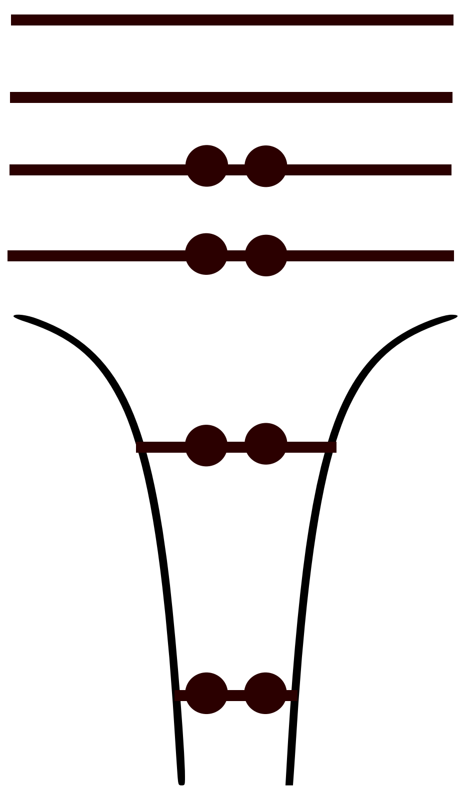


© D. Popova-Gorelova and R. Santra, PRB, 2015, "Imaging instantaneous electron flow with ultrafast resonant x-ray scattering."

Attosecond momentum-resolved RIXS

Hartree-Fock

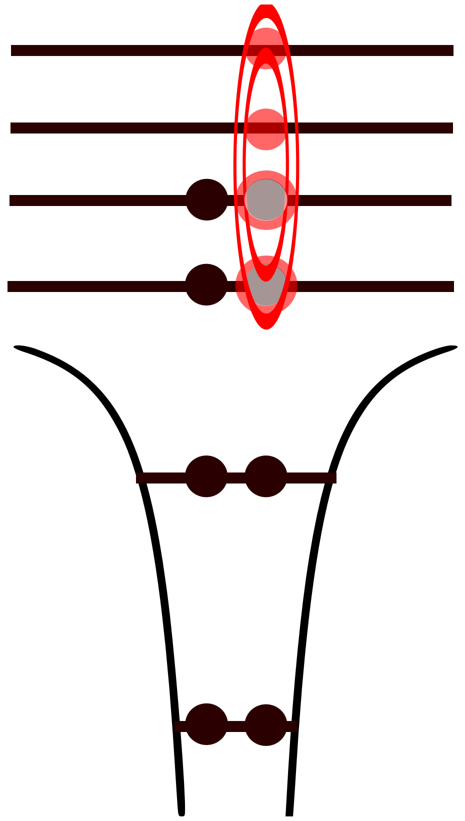
$$|\Psi_0\rangle$$



Ground

Configuration Interaction

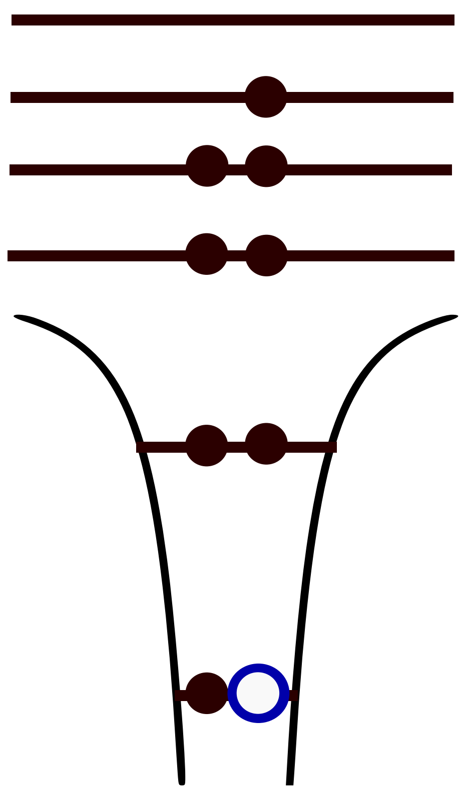
$$\sum_n e^{-i\varepsilon_n t_p}|\Psi_n\rangle$$



Initial superposition

Configuration Interaction + HEXS

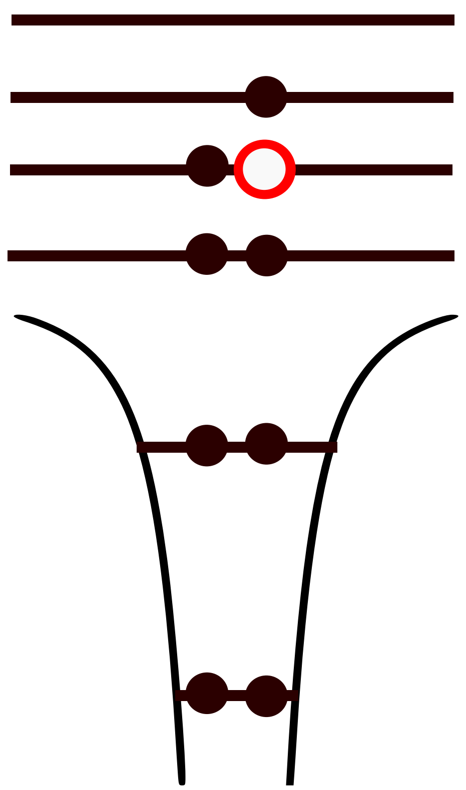
$$|\Psi_J\rangle = \sum_a c_{ja}^{(J)}|\Phi_j^a\rangle$$



Intermediate

Configuration Interaction

$$|\Psi_n\rangle = \sum_{i,a} c_{ia}^{(n)}|\Phi_i^a\rangle$$

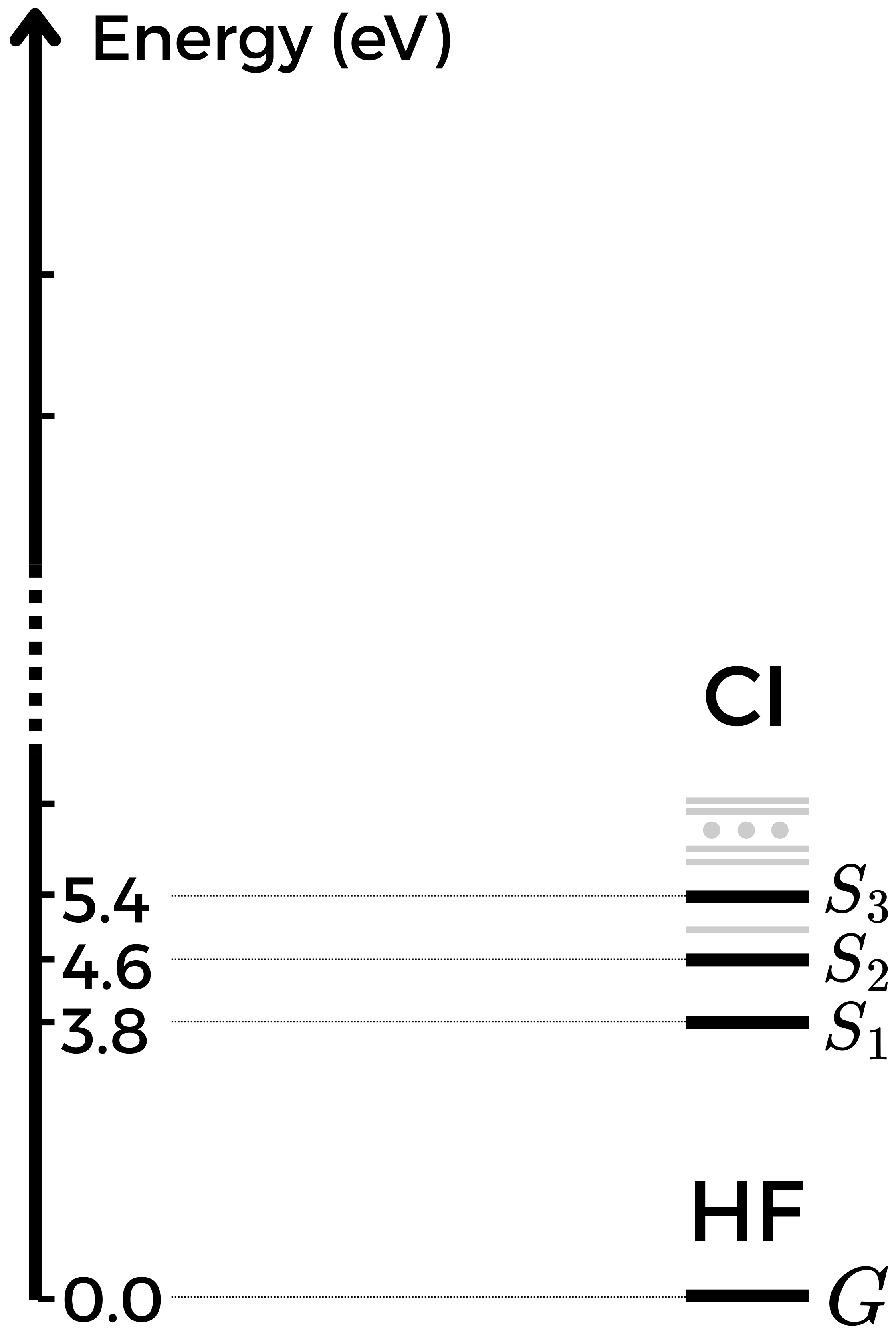


Final

“Attosecond momentum-resolved resonant inelastic x-ray scattering...”

What can be calculated for sexithiophene?
Which parameters can be used?

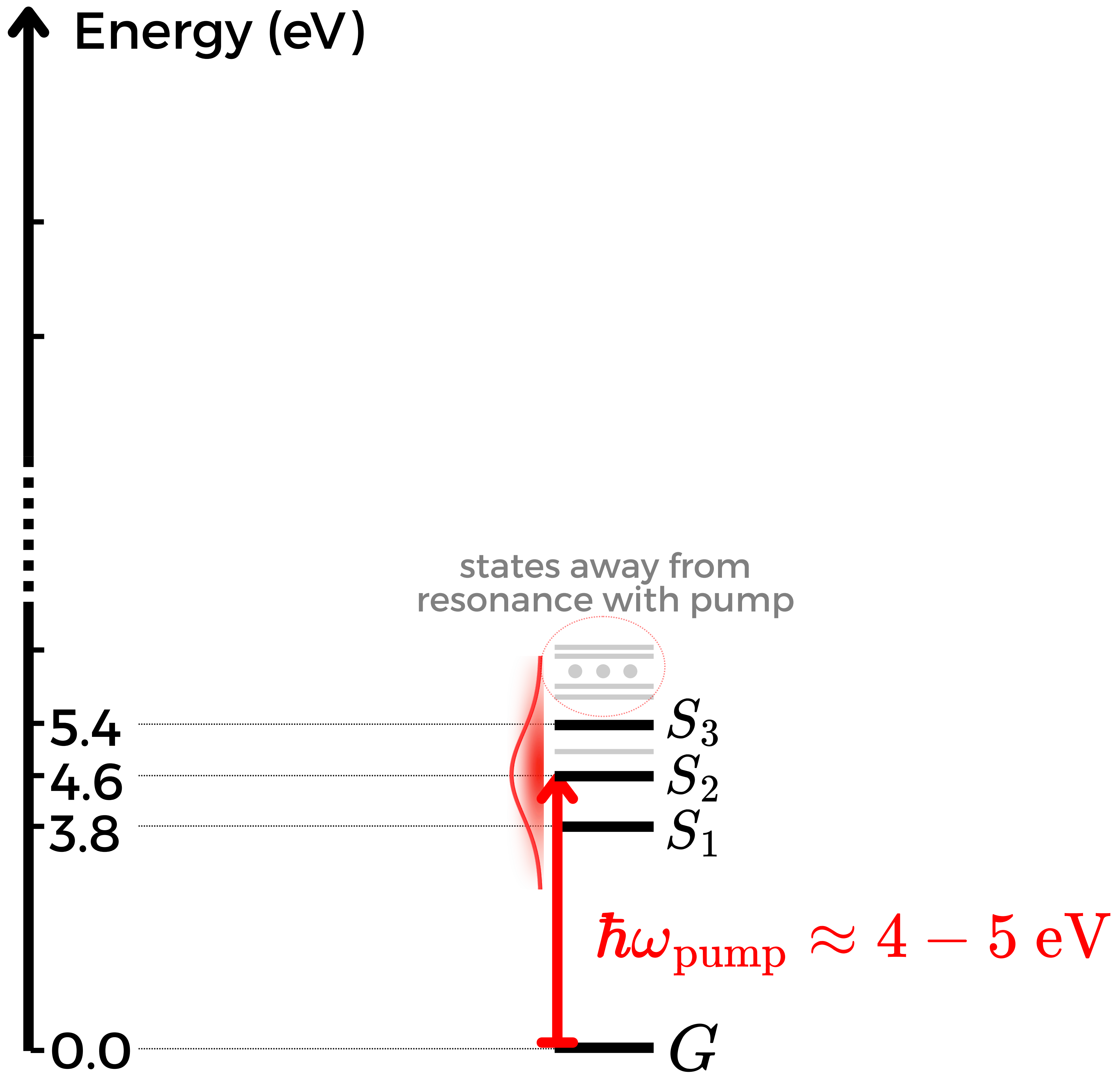
Attosecond momentum-resolved RIXS



Three bright singlet states

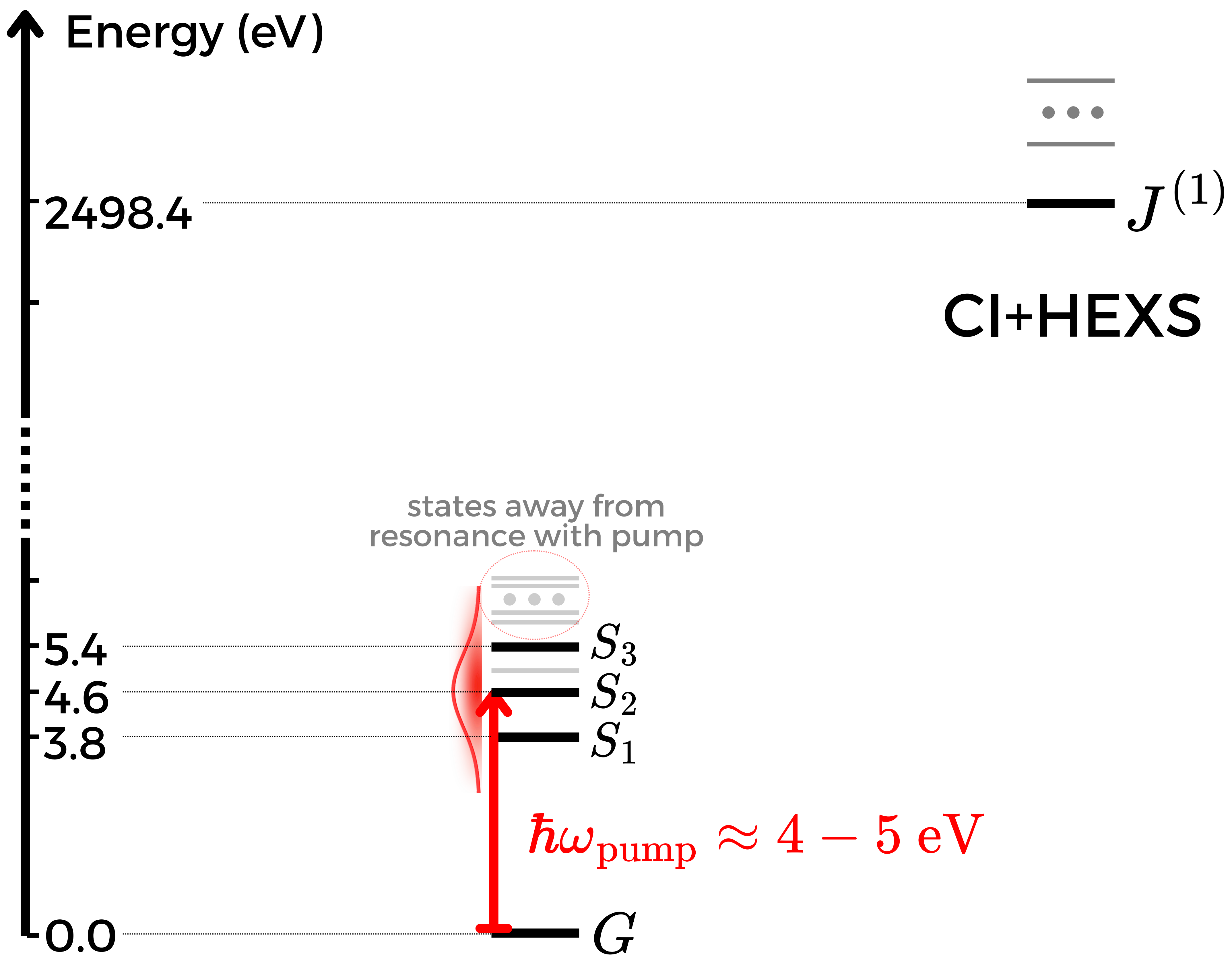
“Attosecond momentum-resolved resonant inelastic x-ray scattering...”

Attosecond momentum-resolved RIXS

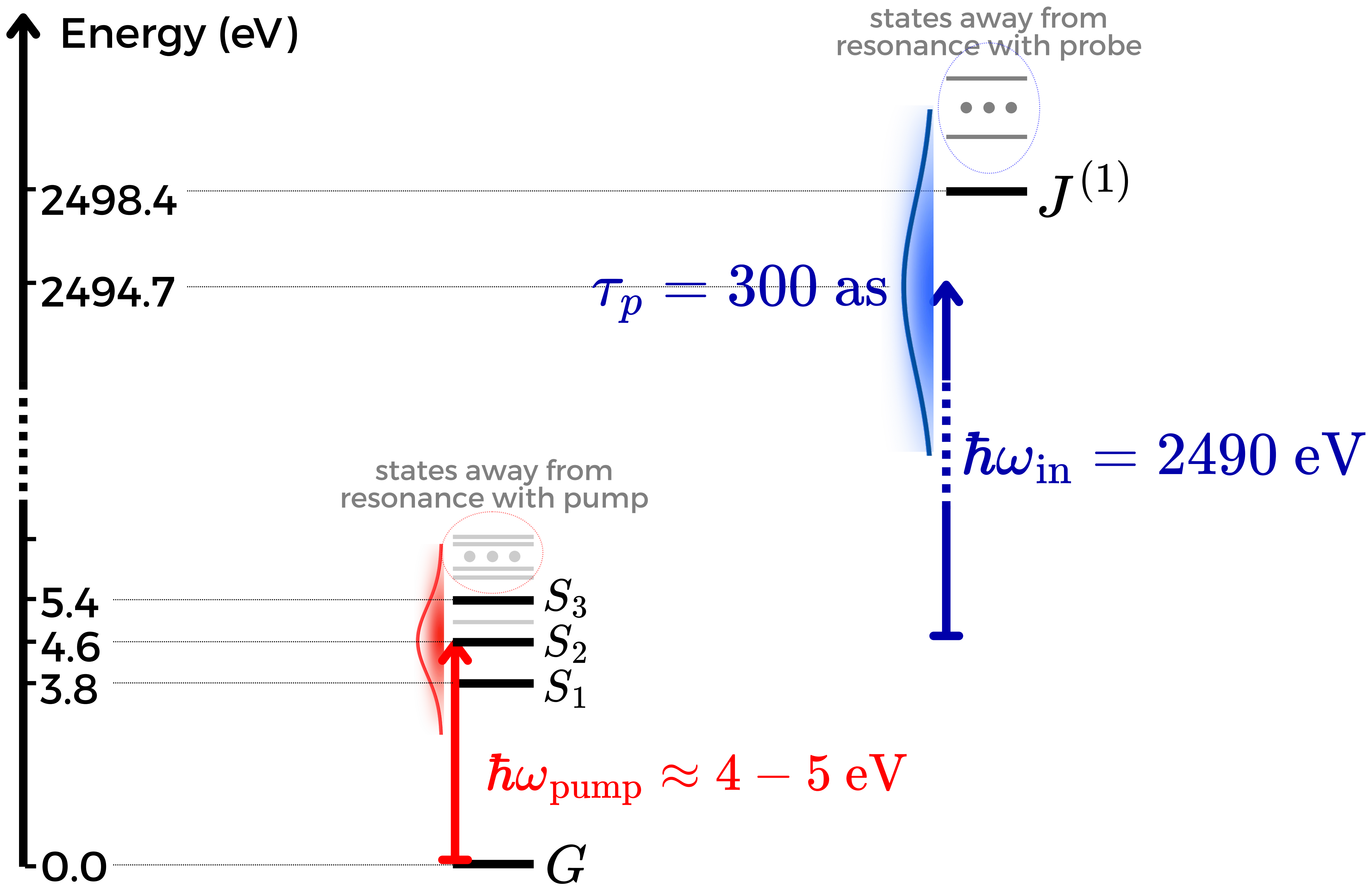


Three bright singlet states

Attosecond momentum-resolved RIXS



Attosecond momentum-resolved RIXS



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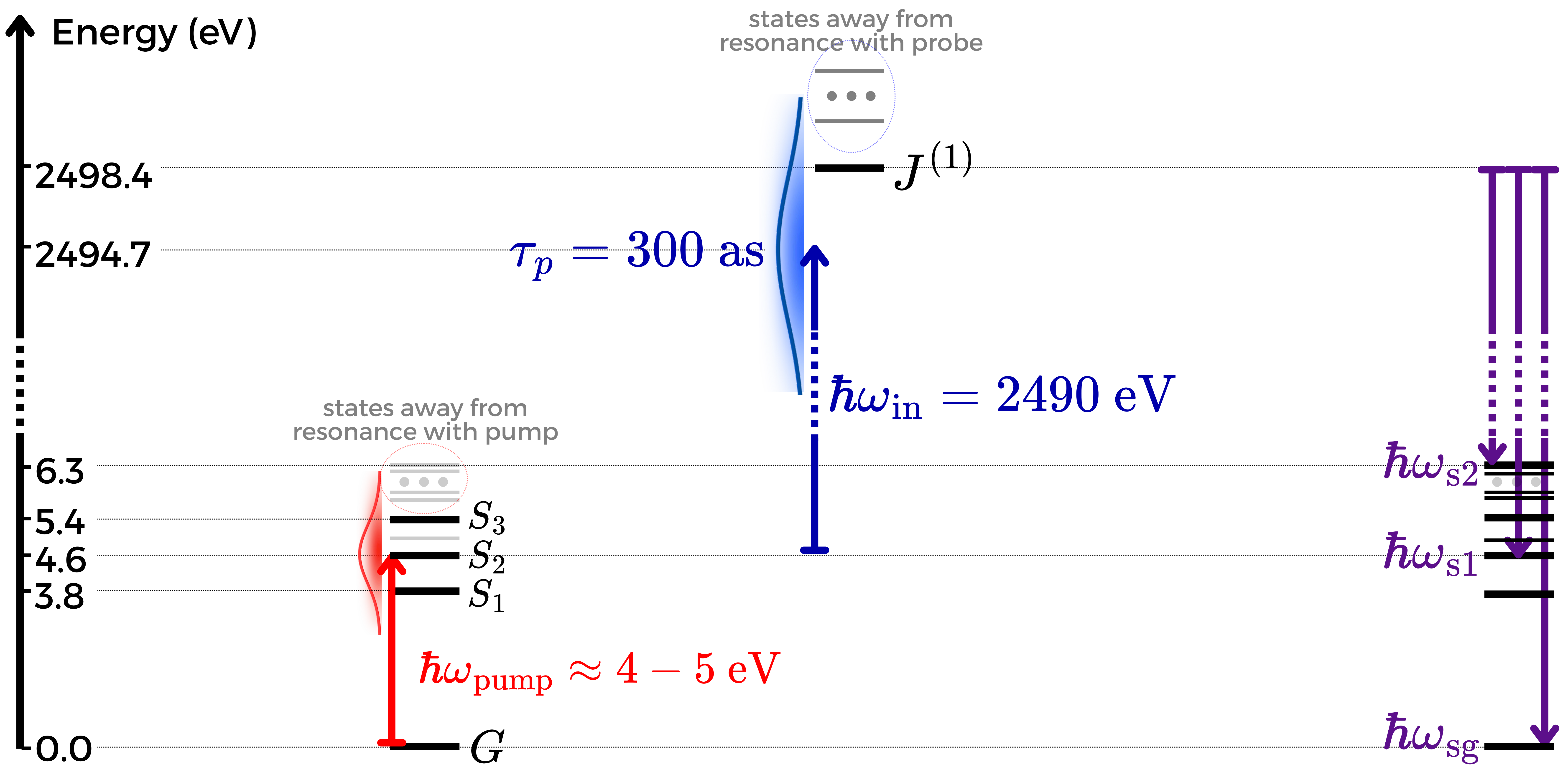

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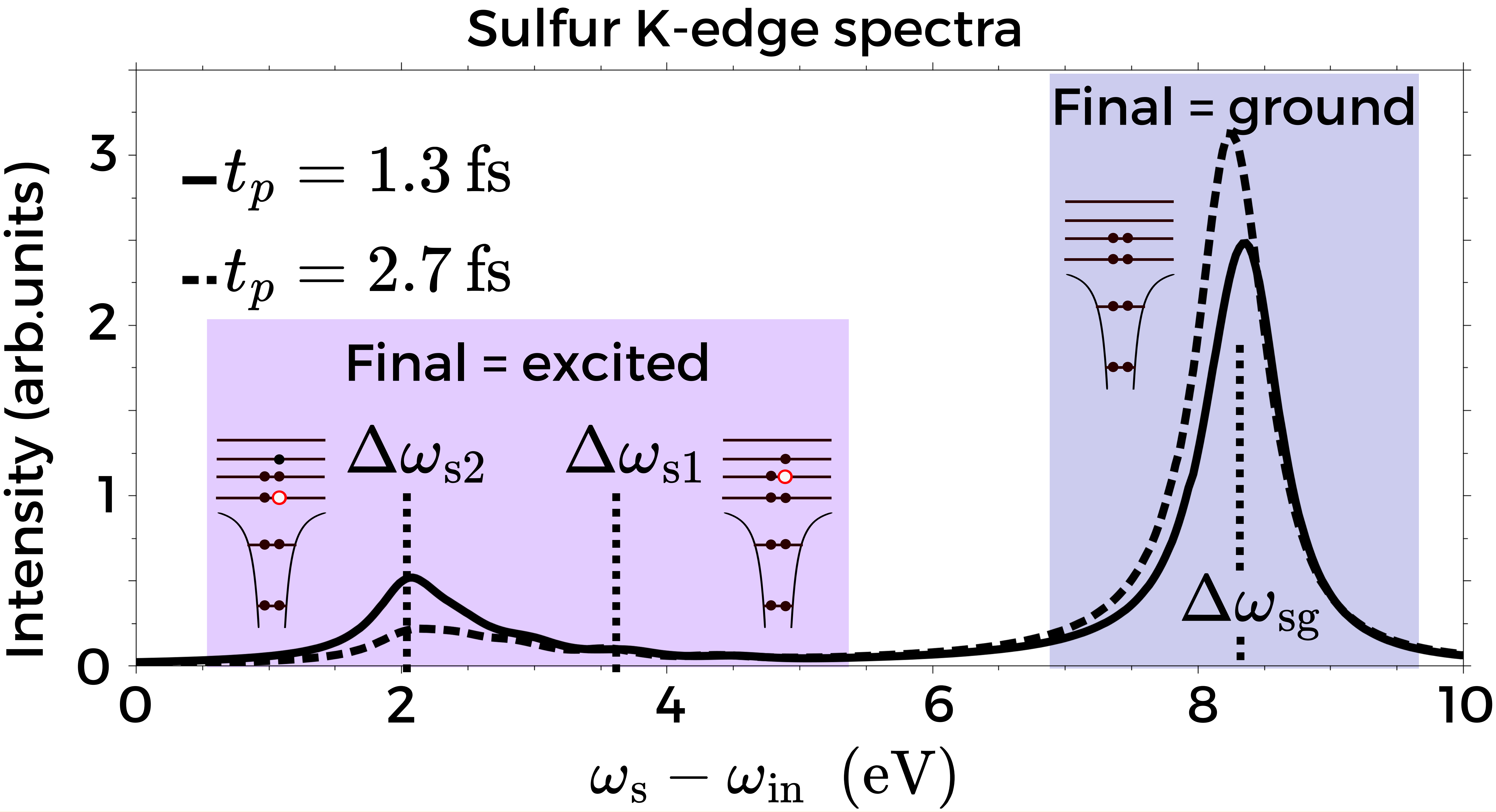
"Attosecond momentum-resolved resonant inelastic x-ray scattering..."

Attosecond ~~momentum-resolved~~ RIXS



"Attosecond momentum-resolved resonant inelastic x-ray scattering..."

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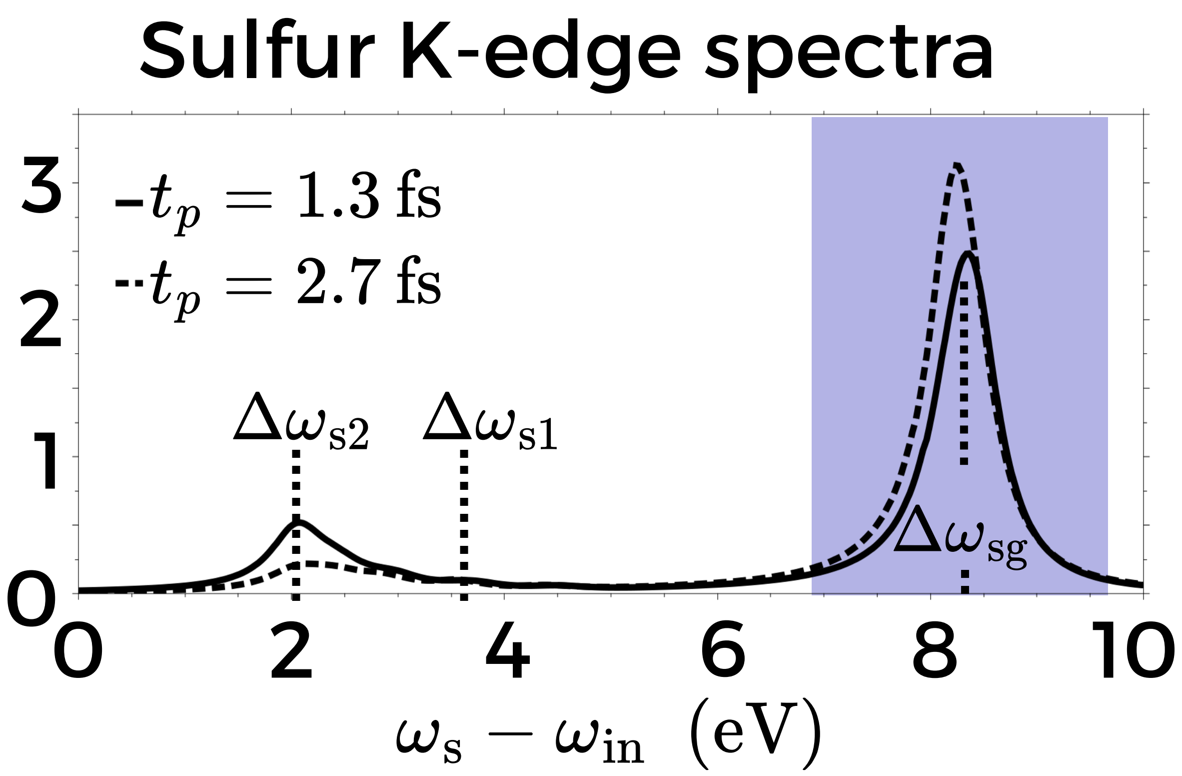

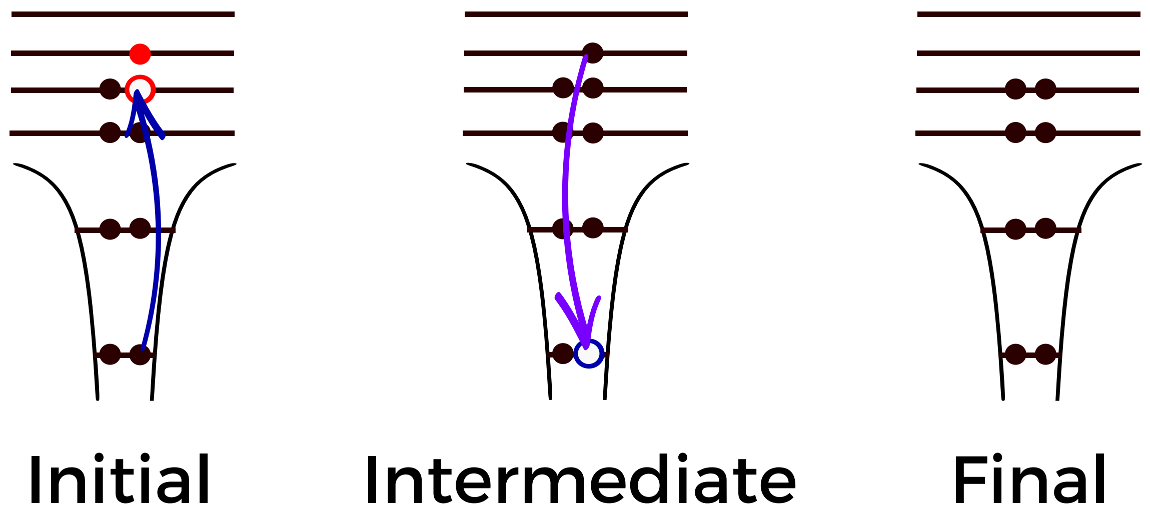

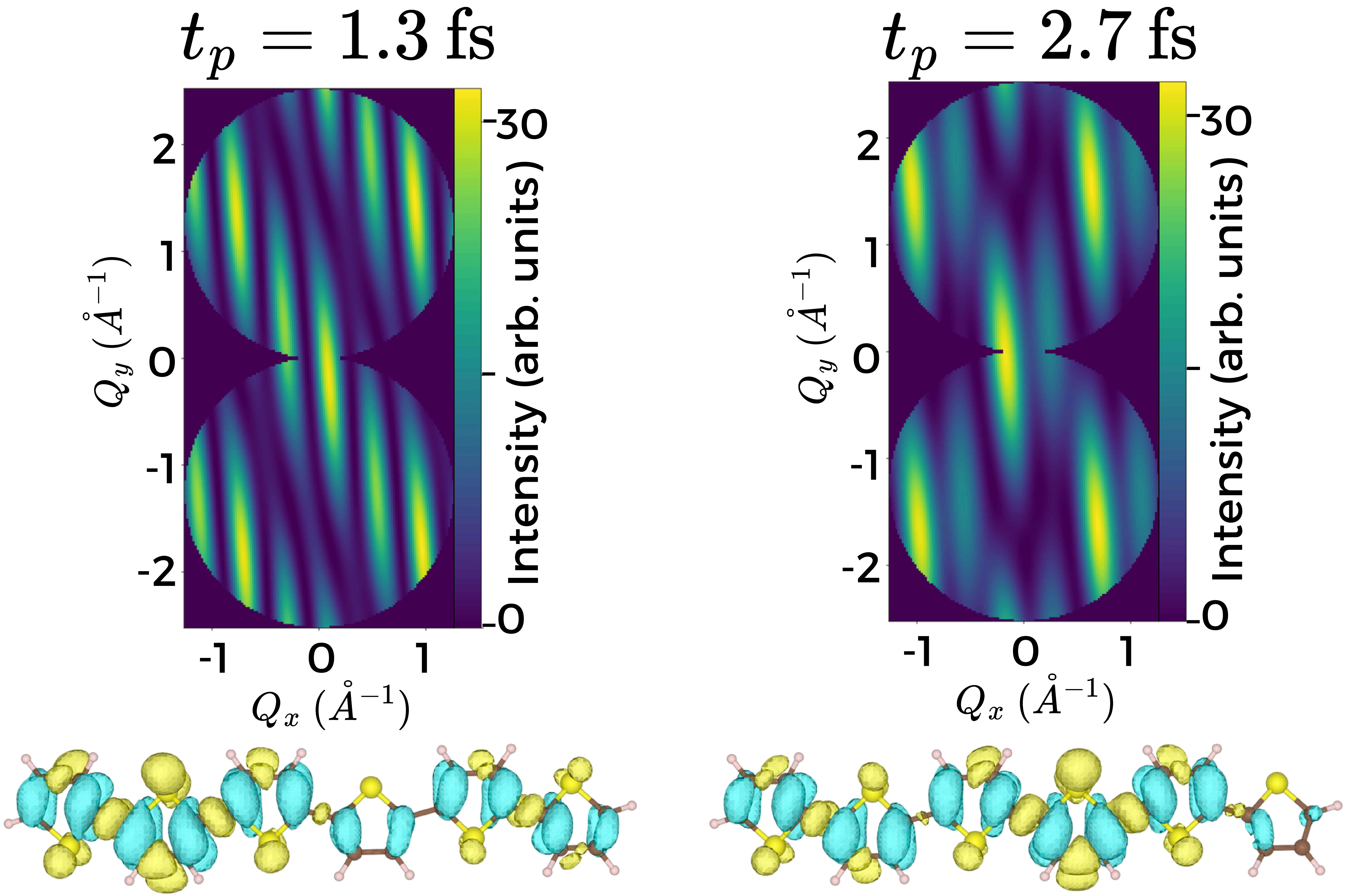

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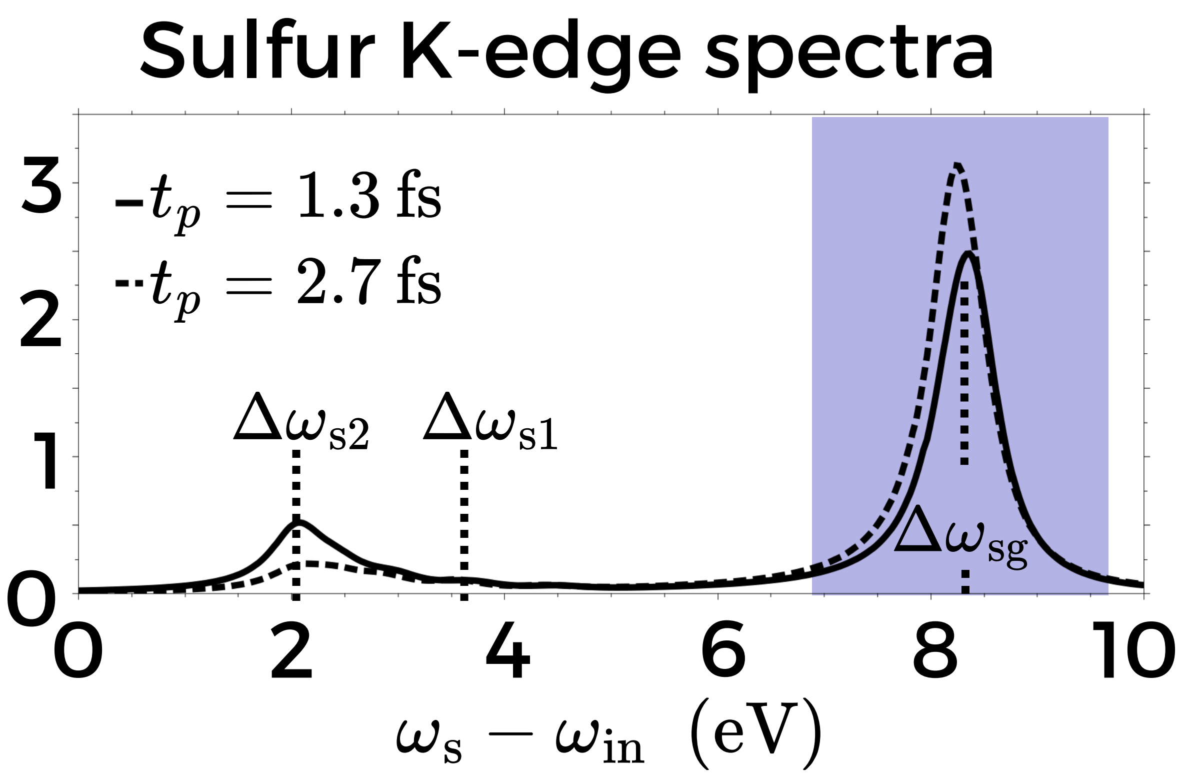

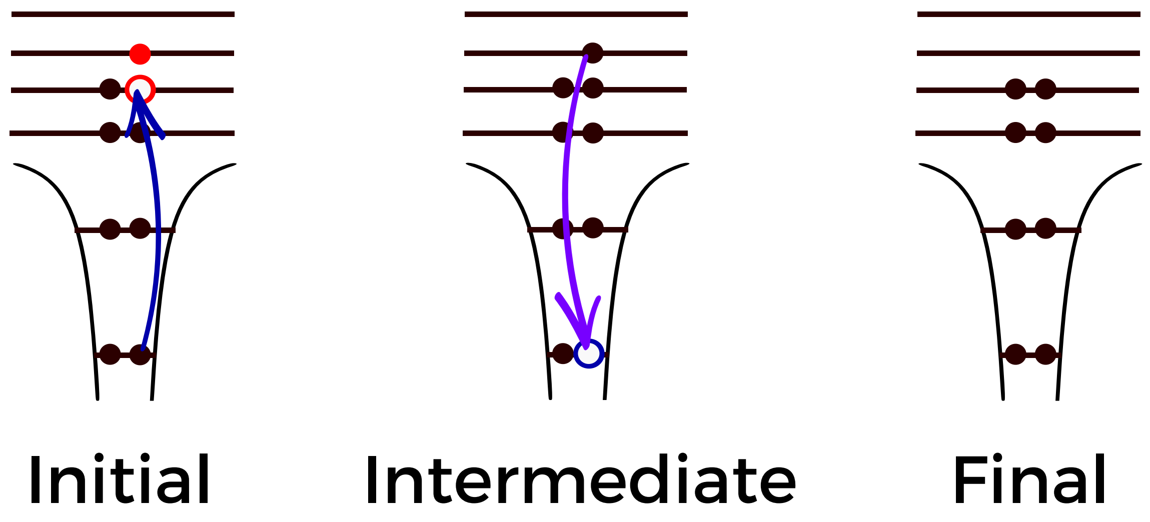

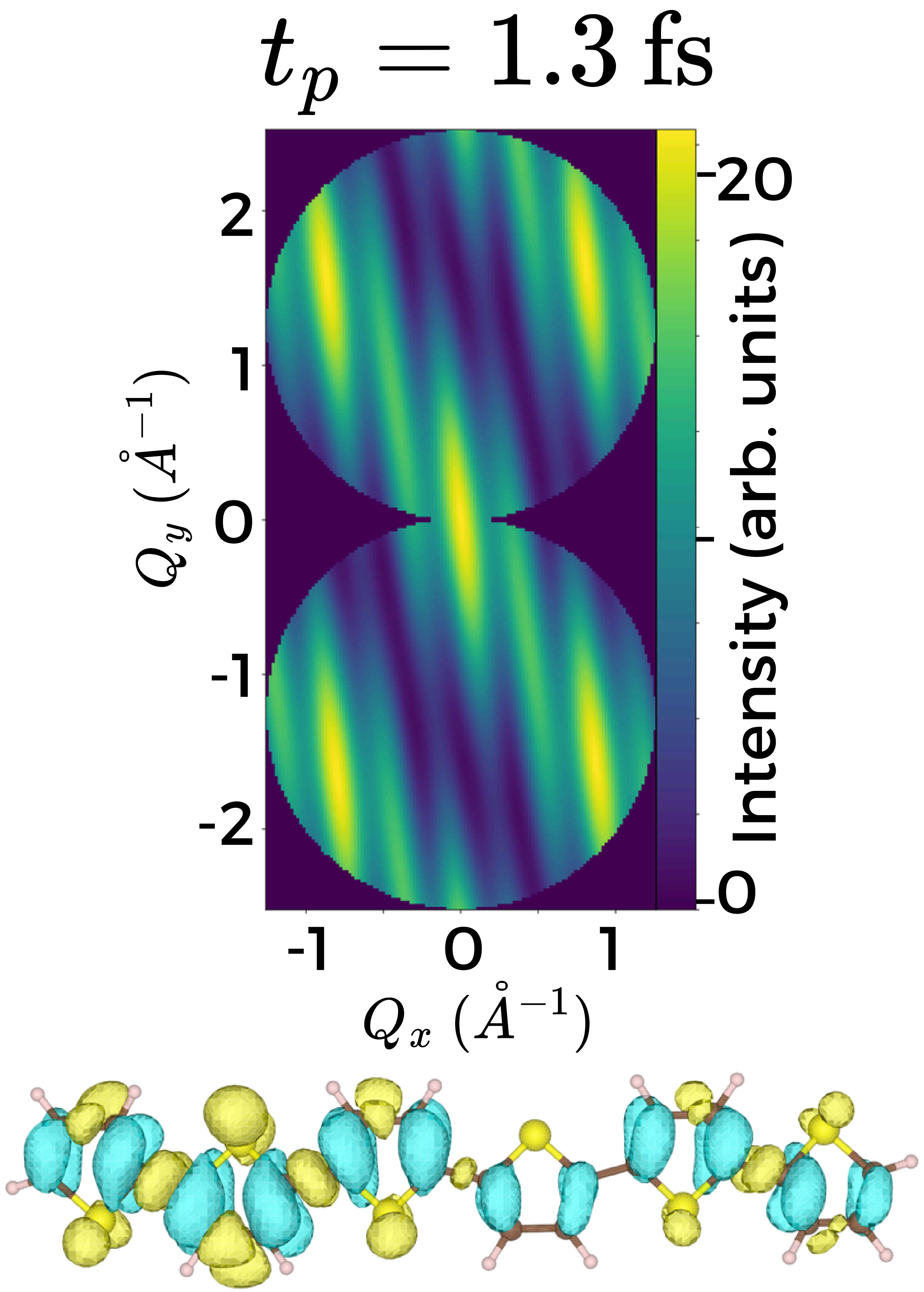

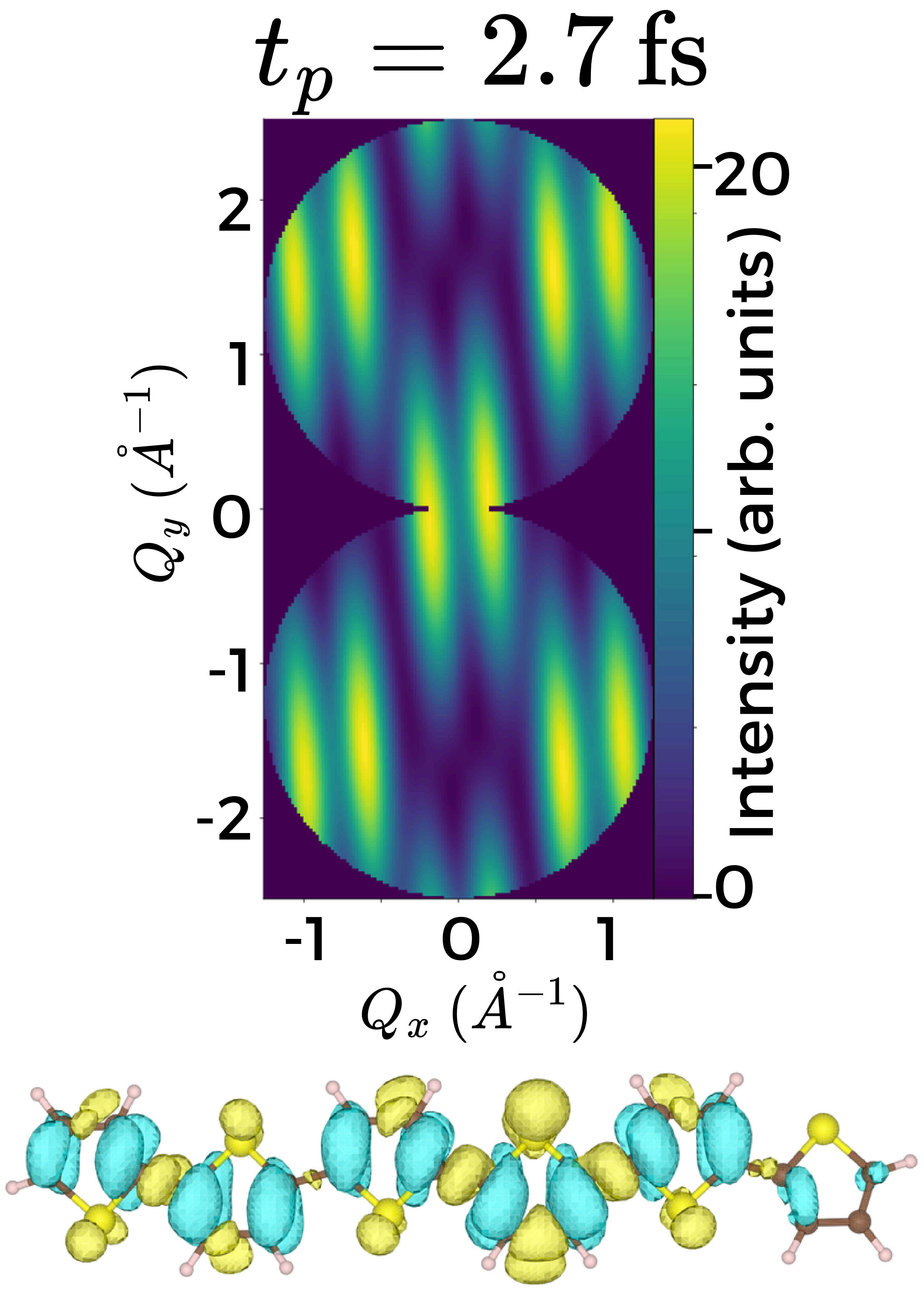

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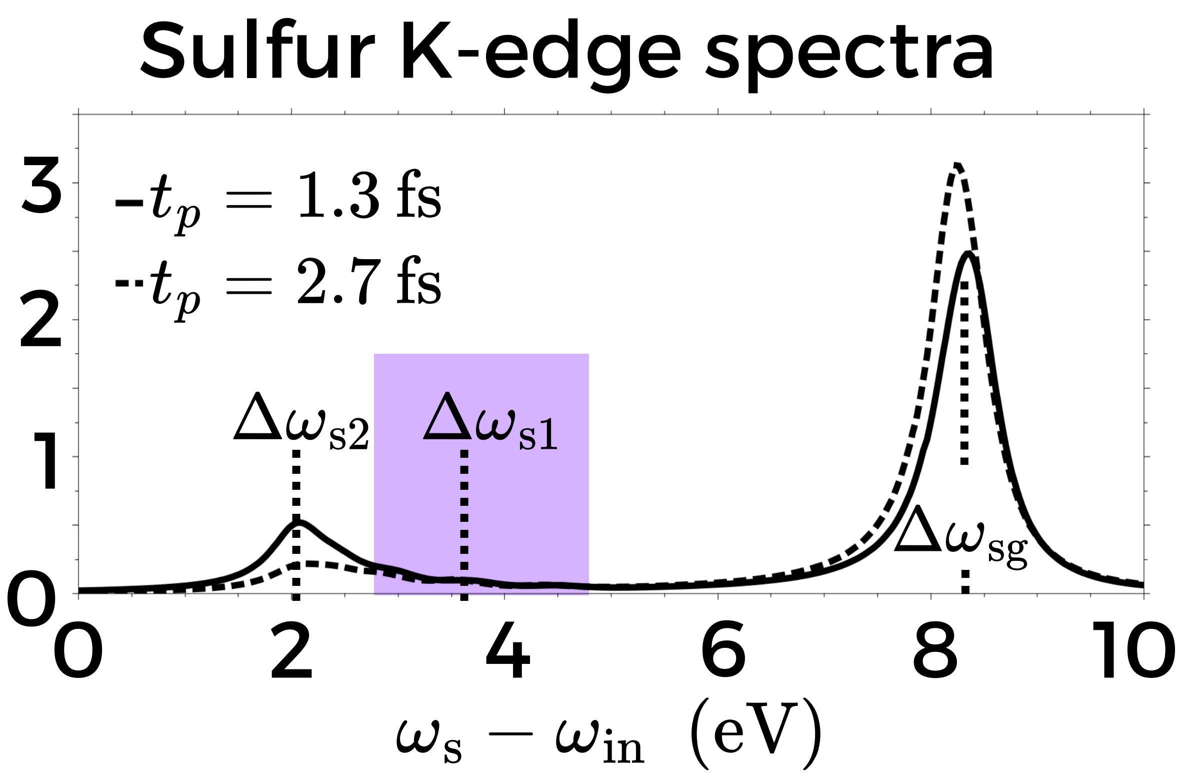
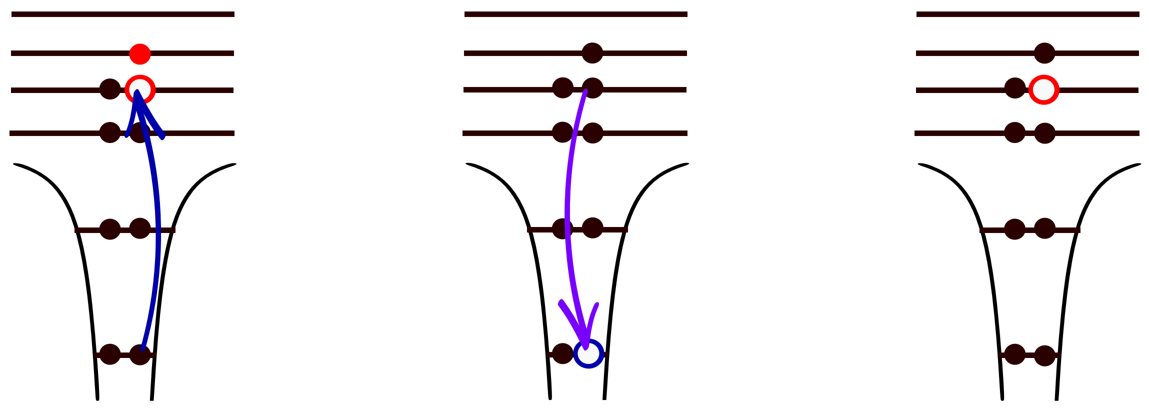
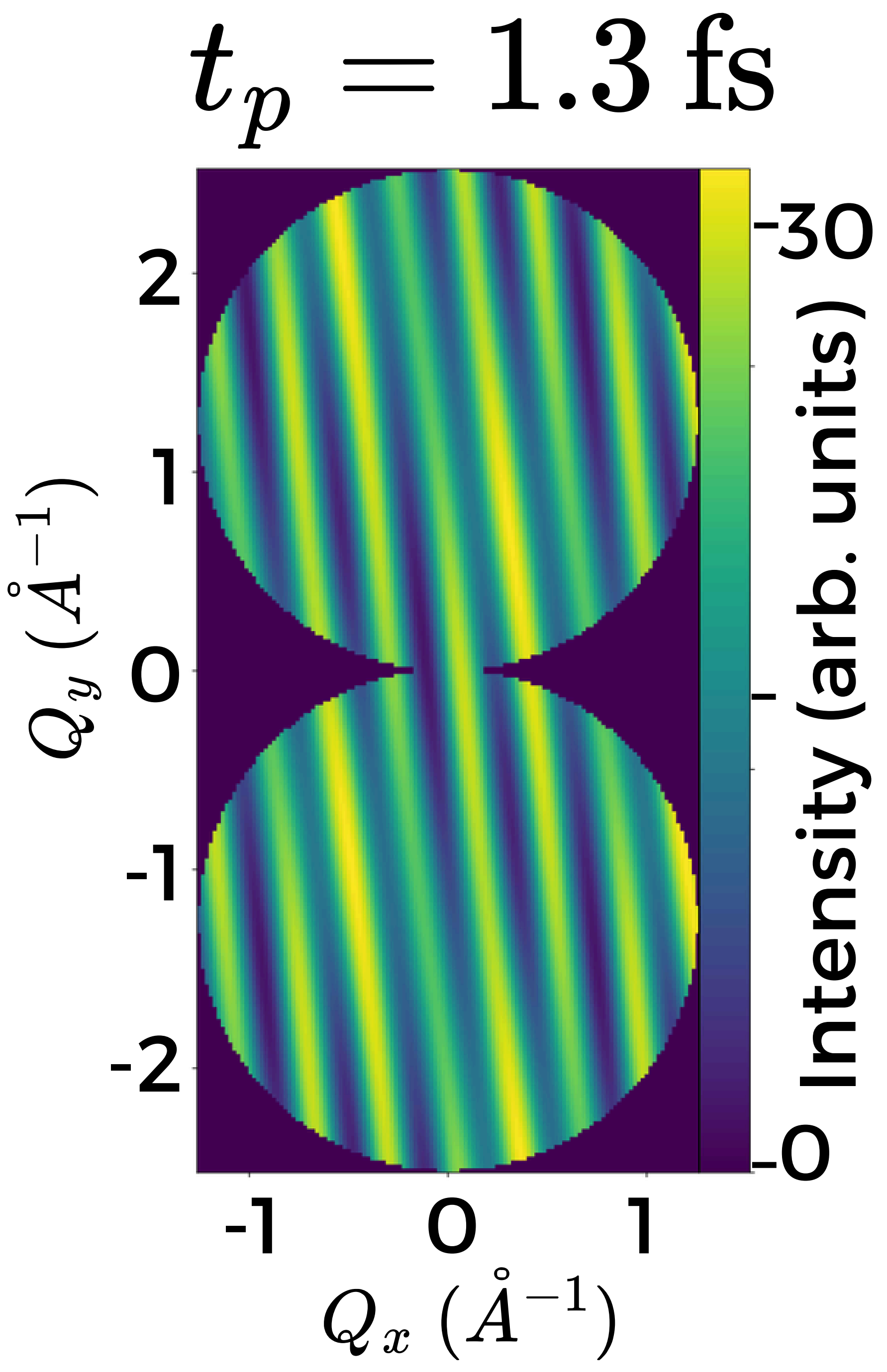
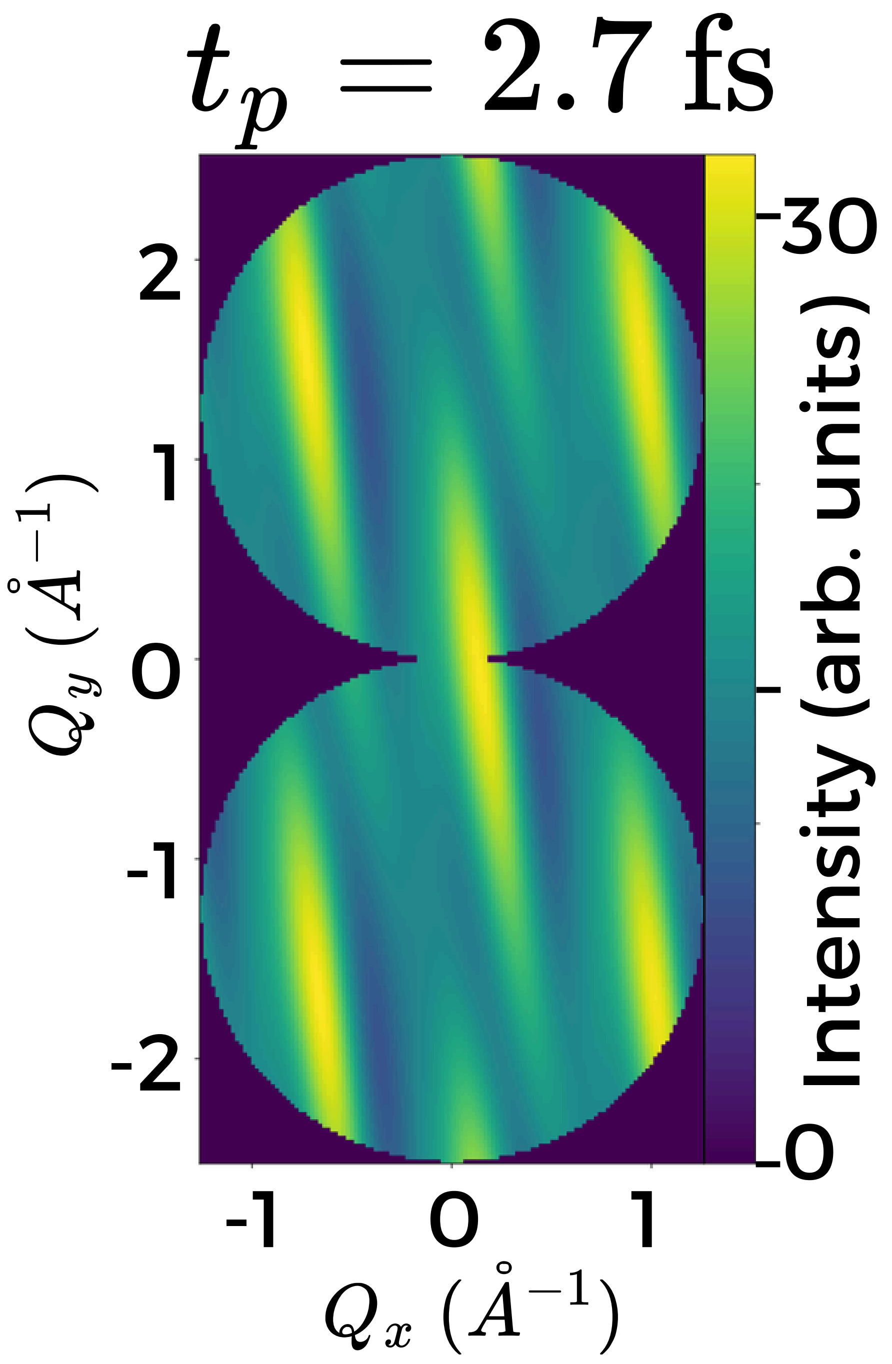
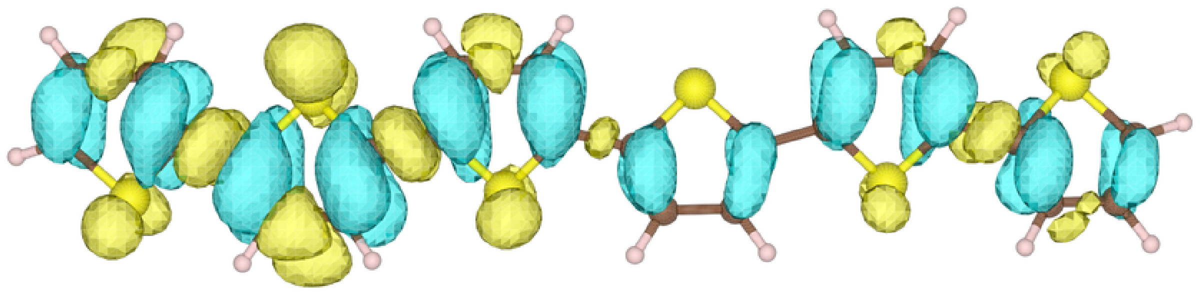
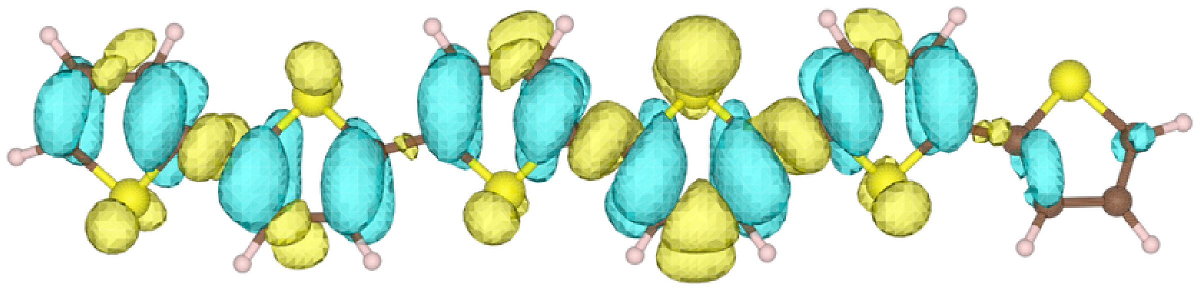








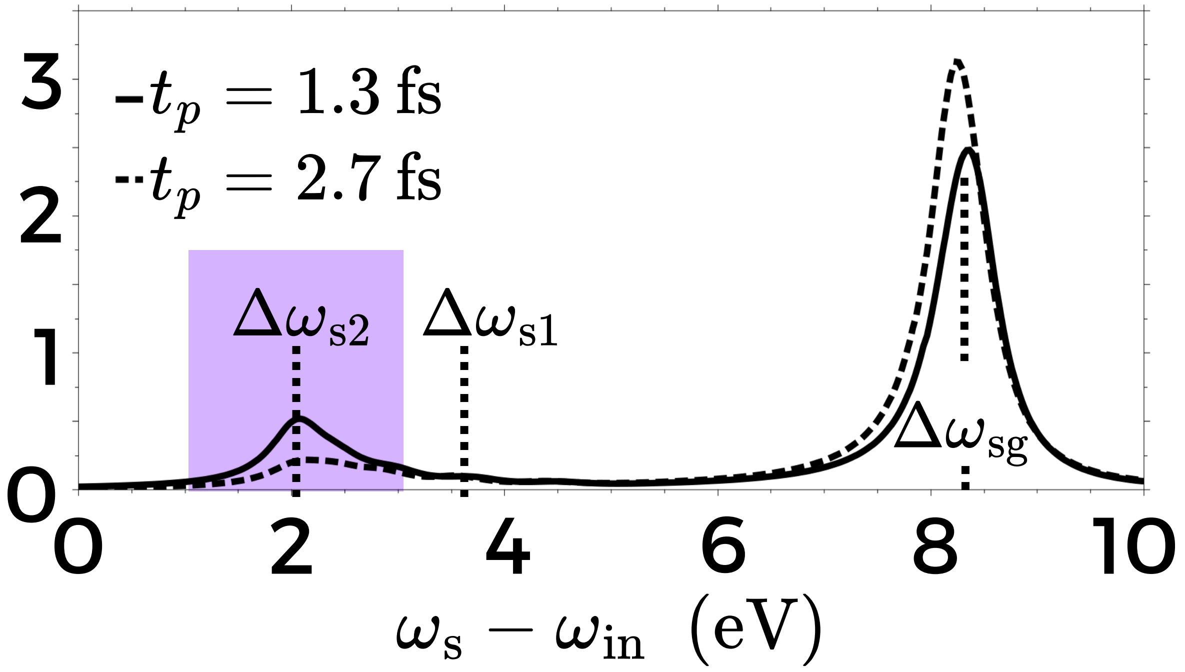


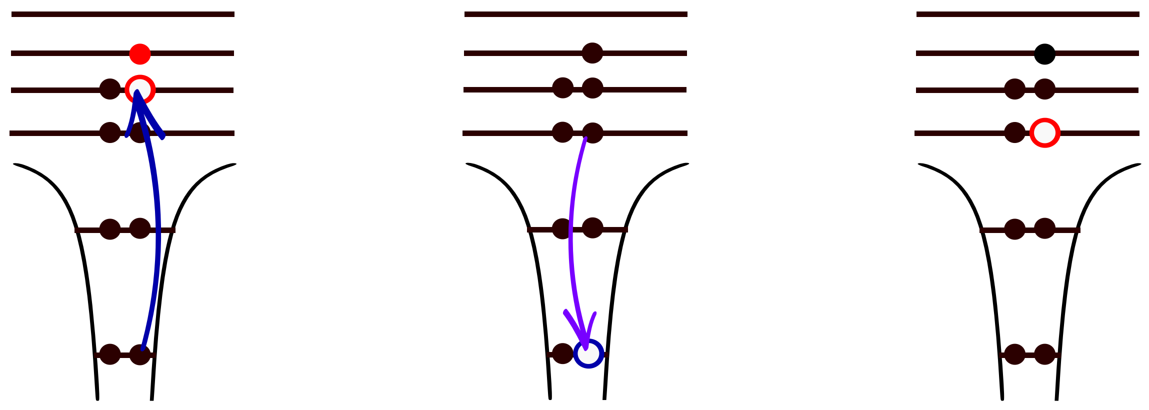


"Attosecond momentum-resolved resonant inelastic x-ray scattering..."

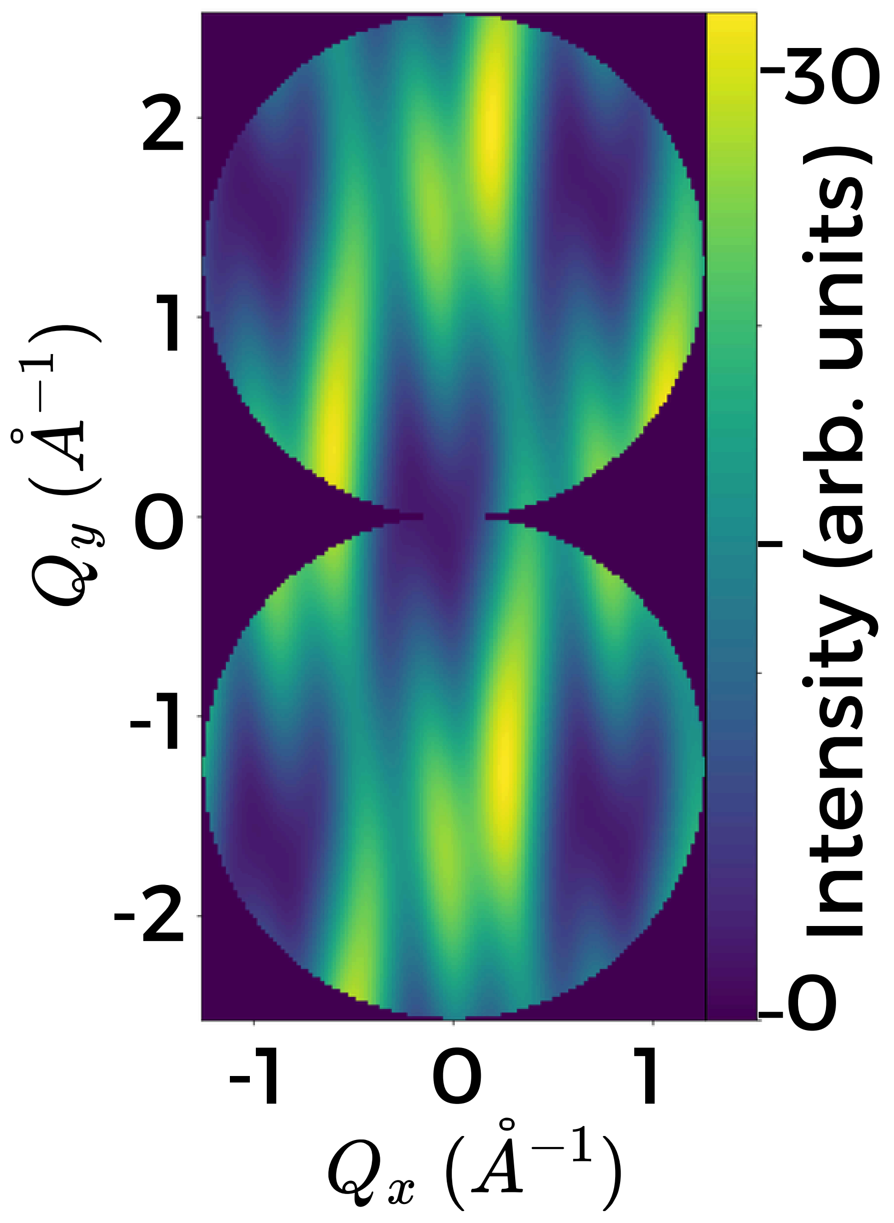
Attosecond momentum-resolved RIXS

Sulfur K-edge spectra

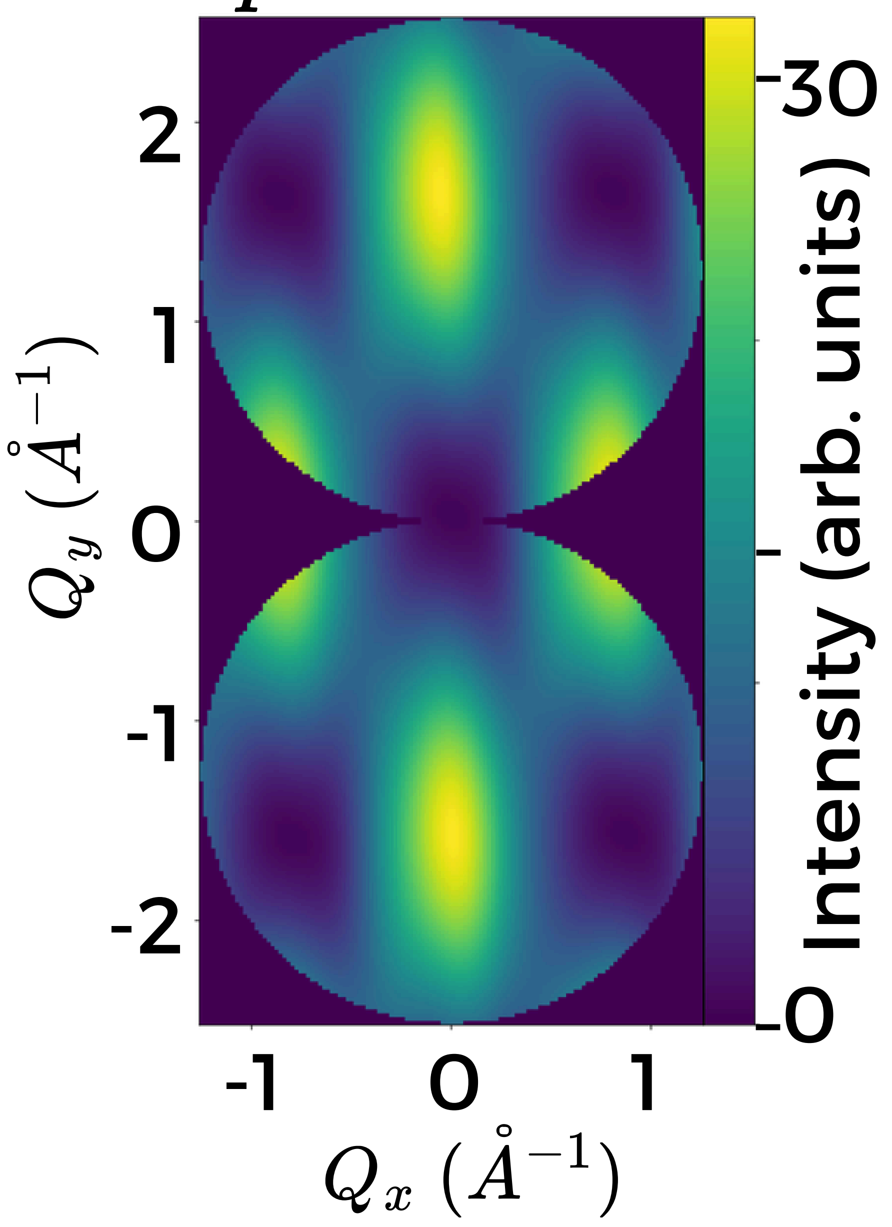


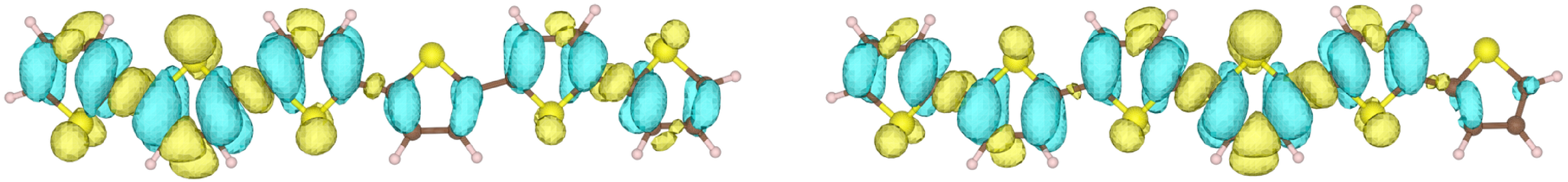


$t_p = 1.3$ fs



$t_p = 2.7$ fs





"Attosecond momentum-resolved resonant inelastic x-ray scattering…"

Can we estimate the signal in experiment?

Attosecond momentum-resolved RIXS

Energy per pulse

$$200[\mu J]$$

Pulse duration

$$300[as]$$

Focus spot

$$1[\mu m^2]$$

Terawatt-attosecond hard X-ray free-electron laser at high repetition rate

Received: 27 May 2024
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Published online: 25 November 2024

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Extreme focusing of hard X-ray free-electron laser pulses enables 7 nm focus width and 10^{22} W cm^{-2} intensity

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The probability to detect photon by pixel (per pulse, per excited molecule)

$$P_p = 5 \cdot 10^{-8}$$

The number of molecules in the focus spot

$$N_{\text{molecules}} = 8 \cdot 10^5$$

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Photons scattered per experiment

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Attosecond momentum-resolved RIXS

Energy per pulse

$$200[\mu J]$$

Pulse duration

$$300[as]$$

Focus spot

$$1[\mu m^2]$$

Repetition rate

$$2.25\ \mathrm{MHz}$$

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Conclusions

01 We propose filming the charge dynamics in molecules with momentum-resolved RIXS.

02 Momentum-resolved RIXS has attosecond temporal and angstrom spatial resolution.

03 It is feasible with the experimental achievements of recent years in FELs.

THANKS FOR WATCHING

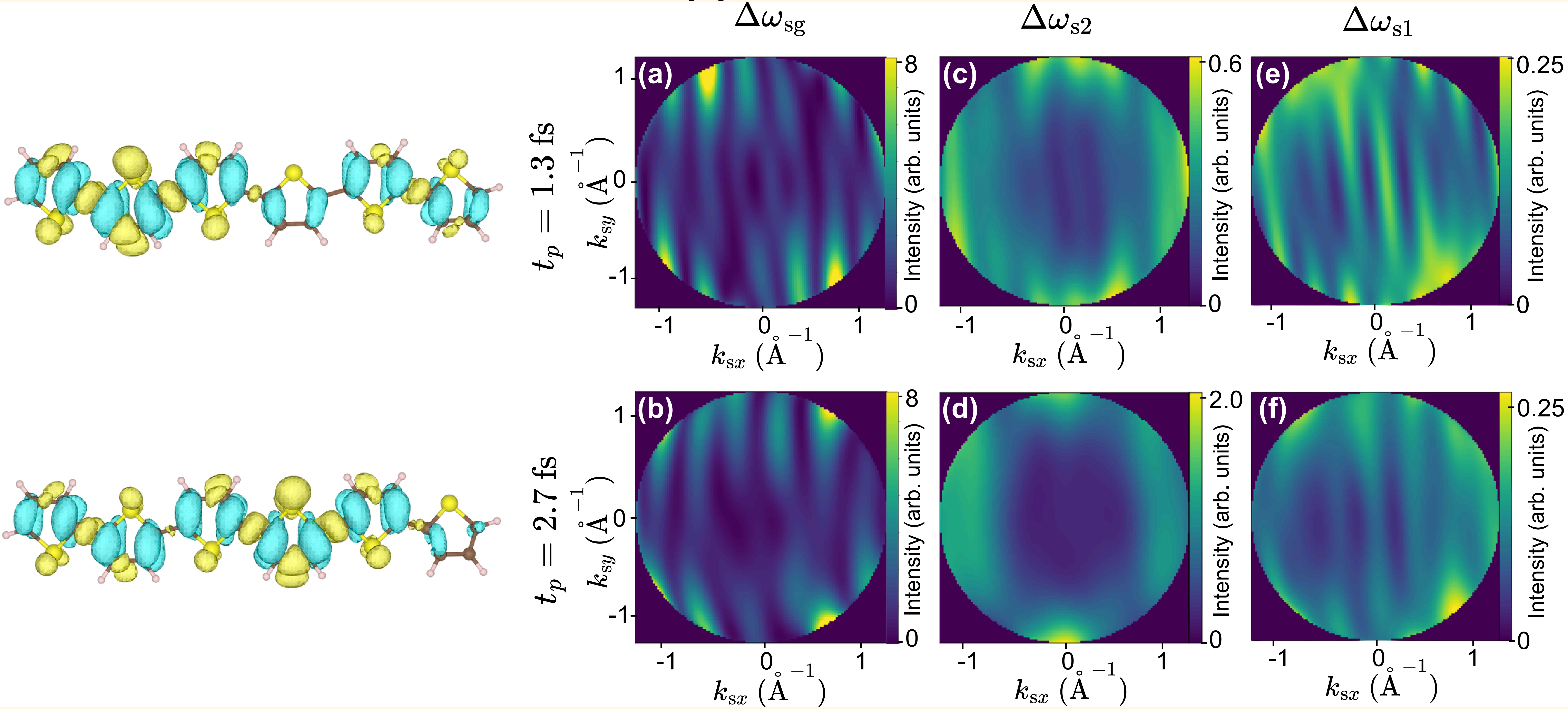
Brandenburgische
Technische Universität
Cottbus - Senftenberg

Supplemental

$$
\begin{aligned}
P(\mathbf{k}_\mathrm{s}, t_p) = \quad & P_\mathrm{e}\,\theta(\mathbf{n}_Q) P_0 \sum_F \frac{1}{\omega_\mathrm{s}} \left| \sum_n C_n e^{-i\varepsilon_n t_p} e^{-\frac{(\varepsilon_F+\omega_\mathrm{s}-\varepsilon_n-\omega_\mathrm{in})^2 \tau_p^2}{8\ln 2}} \sum_{J'} \frac{1}{(\omega_\mathrm{s} + \varepsilon_F - \varepsilon_{J'} + i\frac{\Gamma}{2})} \right. \\
& \times \left(\boldsymbol{\epsilon}_\mathrm{s}^* \cdot \sum_{p_1,q_1} \sum_{N_1,o_1} e^{-i\boldsymbol{k}_\mathrm{s}\boldsymbol{R}_{N_1}} \Xi^*_{p_1,N_1,o_1} \langle \xi_{N_1,o_1} | \boldsymbol{\nabla} | \phi_{q_1} \rangle \langle \Psi_F | \hat{c}^\dagger_{p_1} \hat{c}_{q_1} | \Psi'_{J'} \rangle \right) \\
& \left. \times \left(\boldsymbol{\epsilon}_\mathrm{in} \cdot \sum_{p_2,q_2} \sum_{N_2,o_2} e^{i\boldsymbol{k}_\mathrm{in}\boldsymbol{R}_{N_2}} \Xi_{q_2,N_2,o_2} \langle \phi_{p_2} | \boldsymbol{\nabla} | \xi_{N_2,o_2} \rangle \langle \Psi'_{J'} | \hat{c}^\dagger_{p_2} \hat{c}_{q_2} | \Psi_n \rangle \right) \right|^2
\end{aligned}
$$

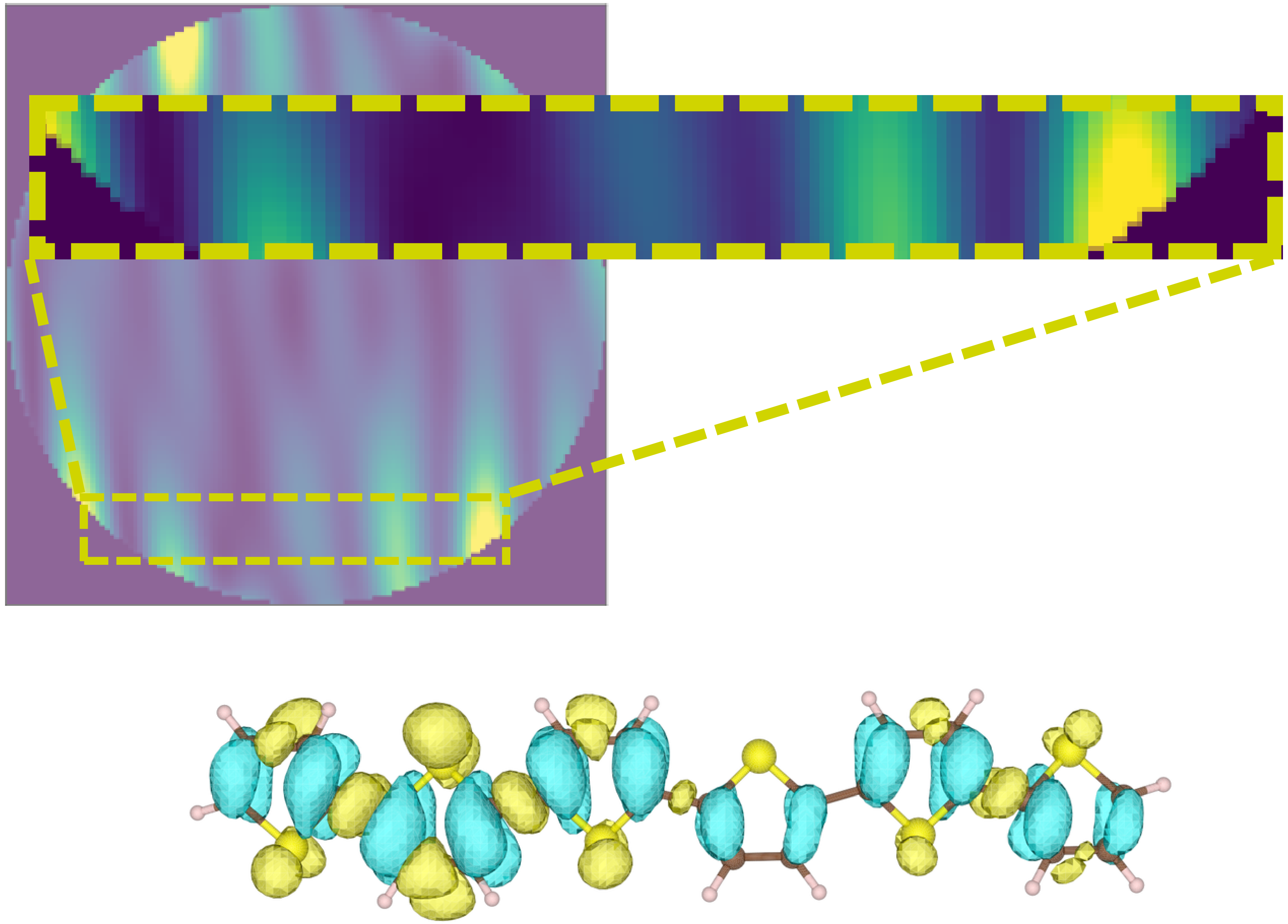
$$
\begin{aligned}
(t_p, \boldsymbol{r}) - \rho_G(\boldsymbol{r}) \quad & = \rho_\mathrm{e}(t_p) + \rho_\mathrm{h}(t_p) = \sum_{m,n} C_m^* C_n e^{i(\varepsilon_m - \varepsilon_n)t_p} \sum_{p,q} \langle \Psi_m | \hat{c}_p^\dagger \hat{c}_q | \Psi_n \rangle \phi_p^*(\boldsymbol{r}) \phi_q(\boldsymbol{r}) - \sum_{p\in\mathrm{HOMOs}} |\phi_p(\boldsymbol{r})|^2 \\
\rho_\mathrm{e}(t_p) \quad & = 2\Re \left(\sum_{m,n\geq m} C_m^* C_n e^{i(\varepsilon_m - \varepsilon_n)t_p} \sum_{p,q\in\mathrm{LUMOs}} \langle \Psi_m | \hat{c}_p^\dagger \hat{c}_q | \Psi_n \rangle \phi_p^*(\boldsymbol{r}) \phi_q(\boldsymbol{r}) \right), \\
\rho_\mathrm{h}(t_p) \quad & = 2\Re \left(\sum_{m,n\geq m} C_m^* C_n e^{i(\varepsilon_m - \varepsilon_n)t_p} \sum_{p,q\in\mathrm{HOMOs}} \langle \Psi_m | \hat{c}_p^\dagger \hat{c}_q | \Psi_n \rangle \phi_p^*(\boldsymbol{r}) \phi_q(\boldsymbol{r}) \right) - \sum_{p\in\mathrm{HOMOs}} |\phi_p(\boldsymbol{r})|^2
\end{aligned}
$$

Supplemental

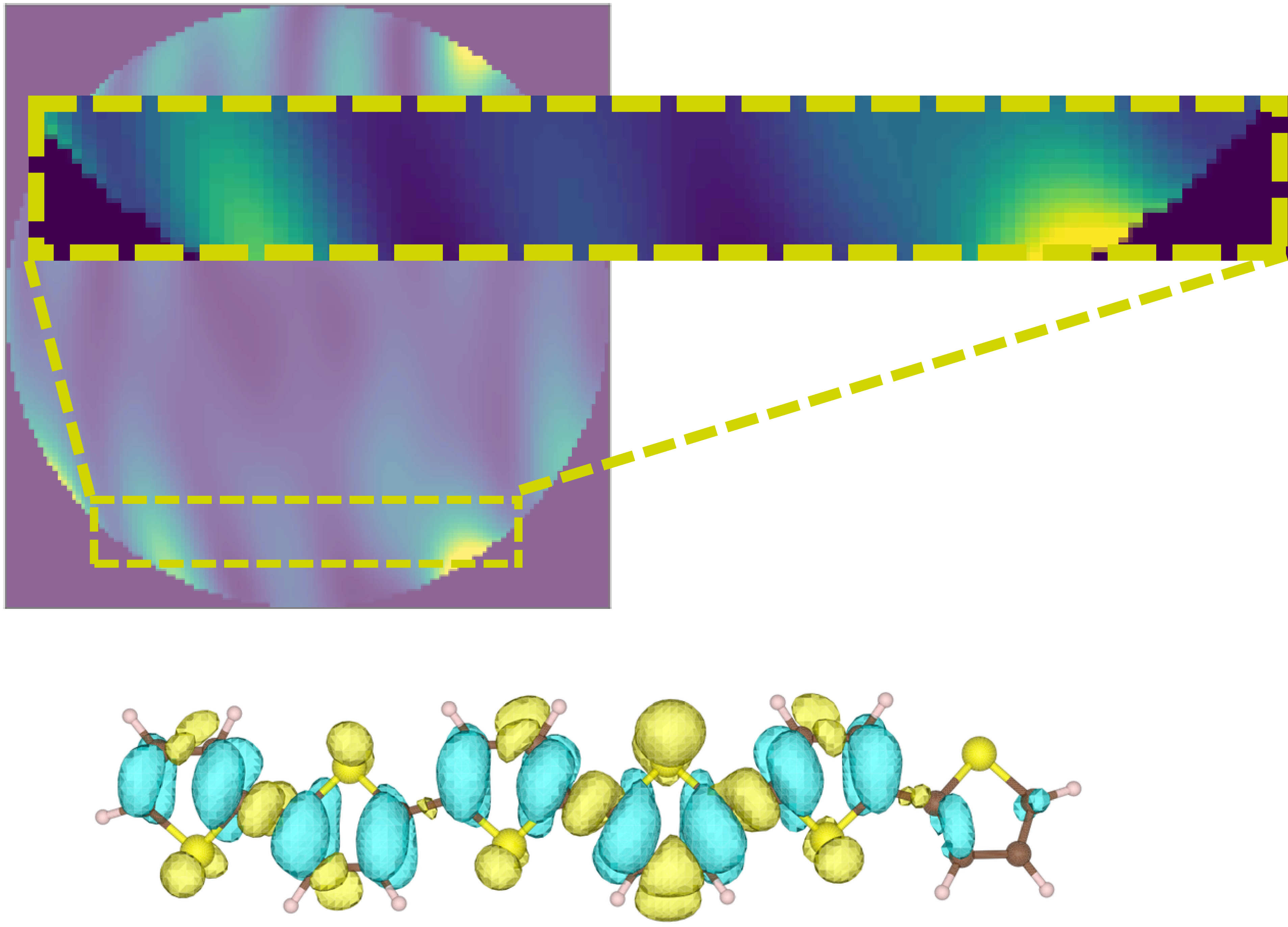


Supplemental

$t_p = 1.3\,\mathrm{fs}$



$t_p = 2.7\,\mathrm{fs}$



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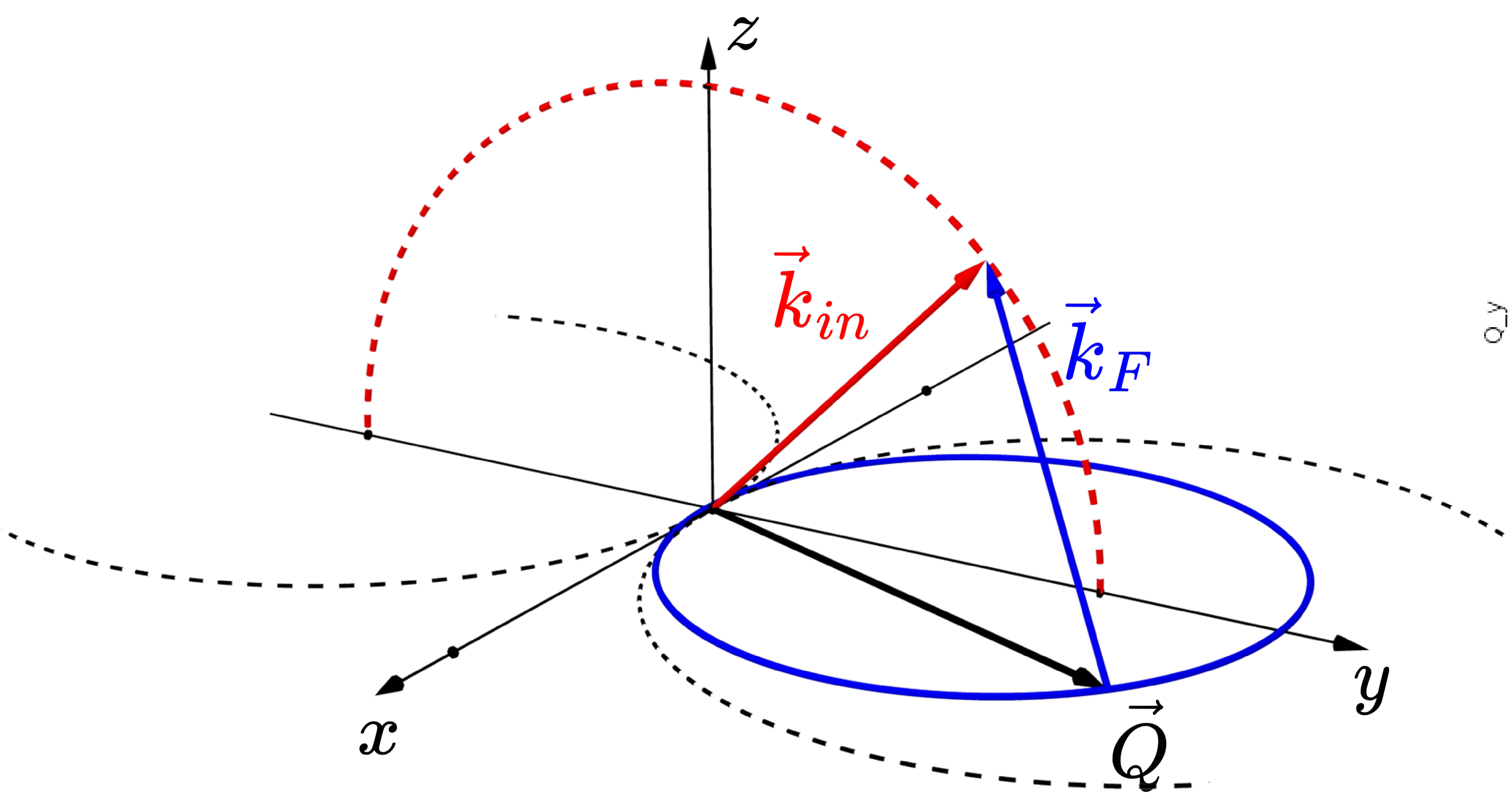

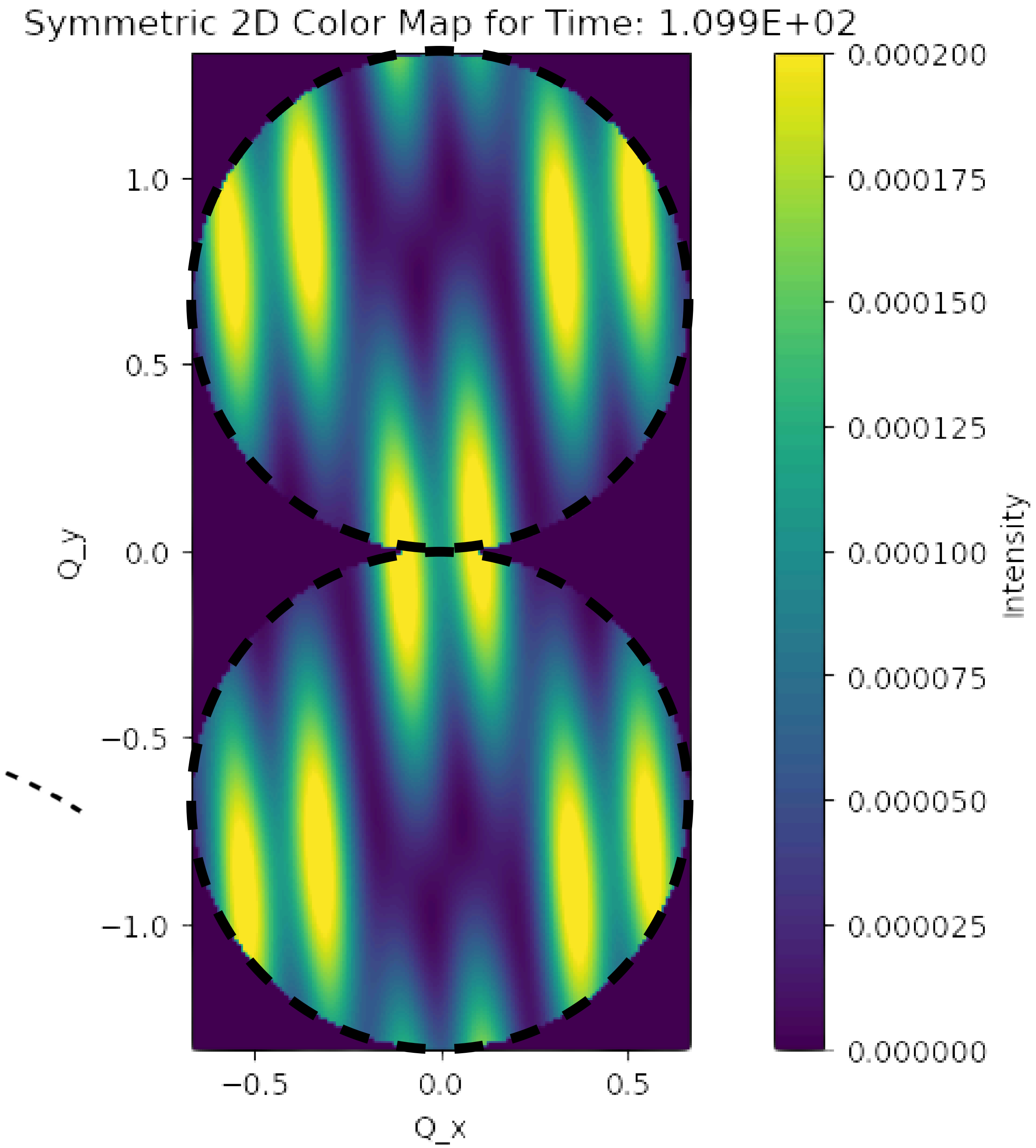

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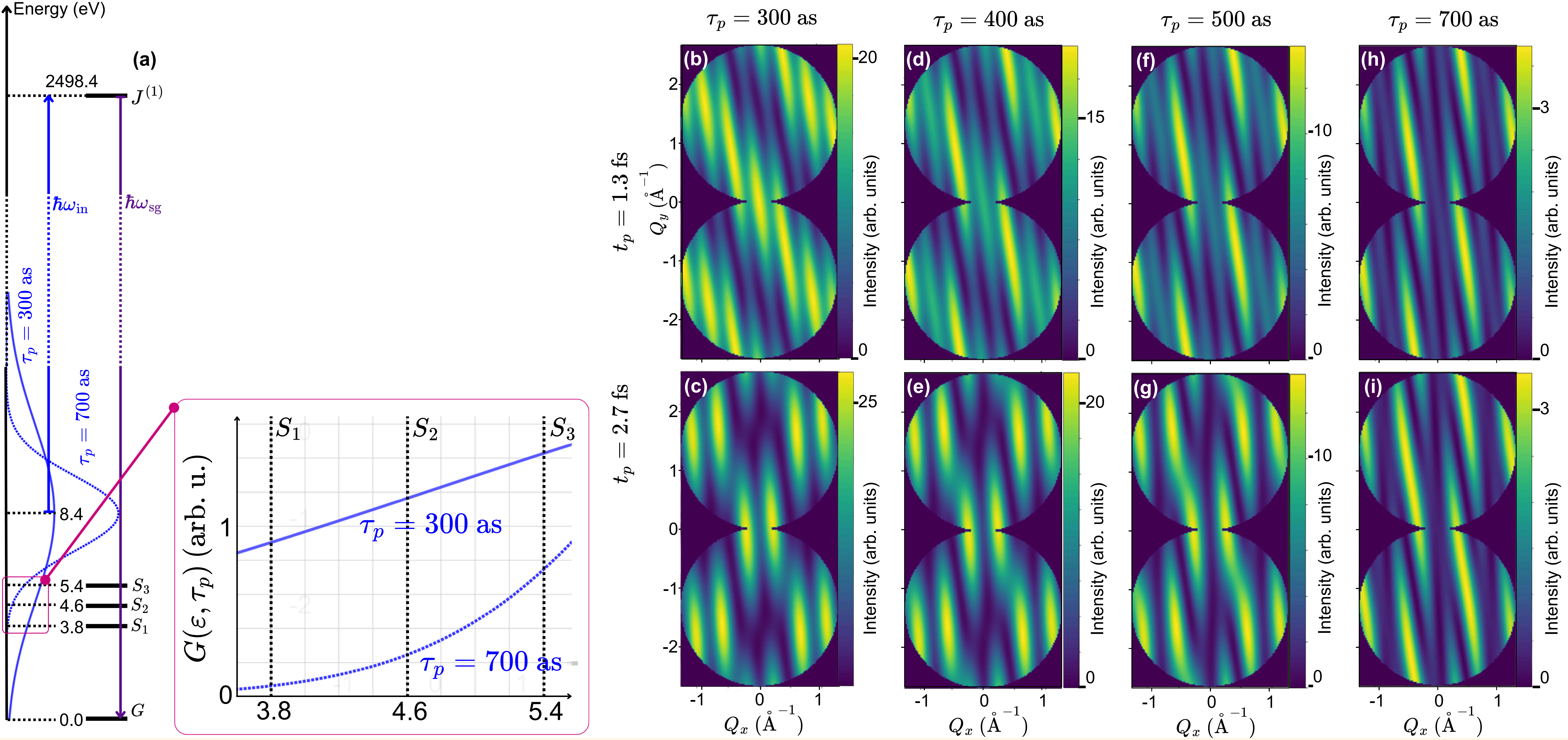
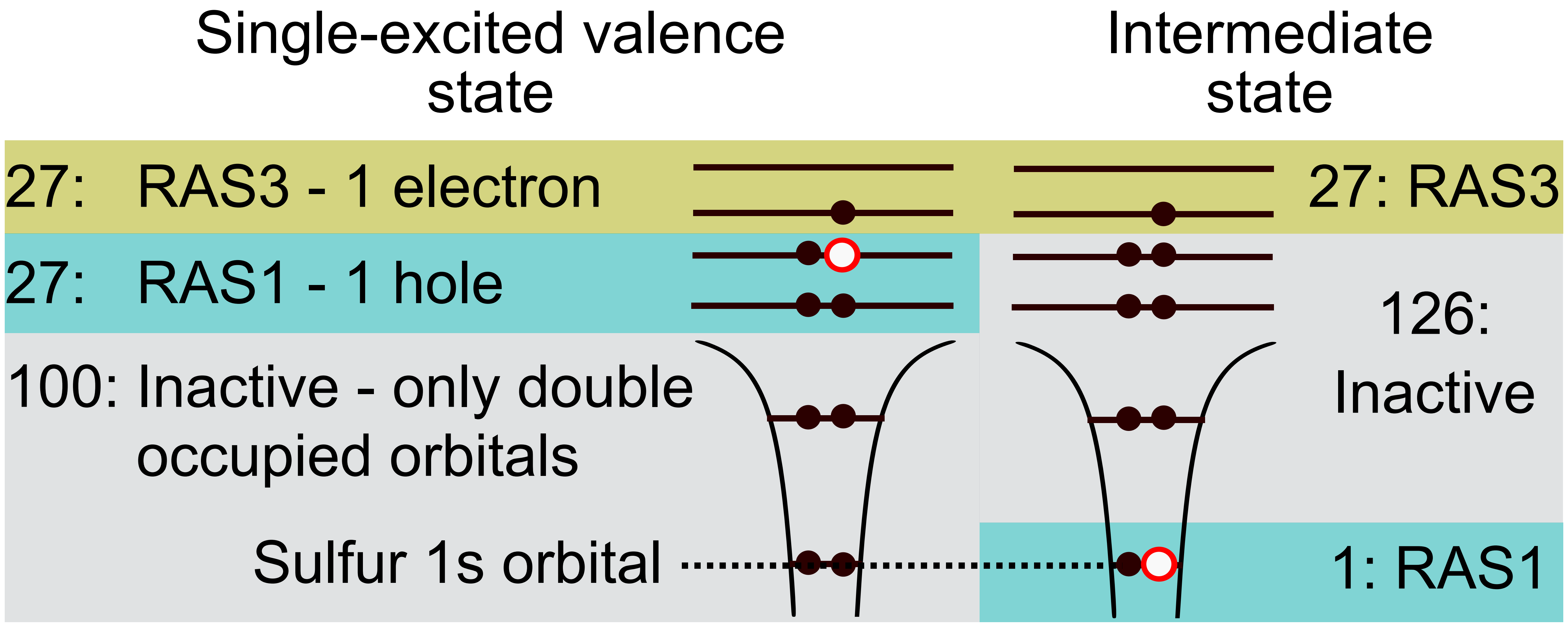
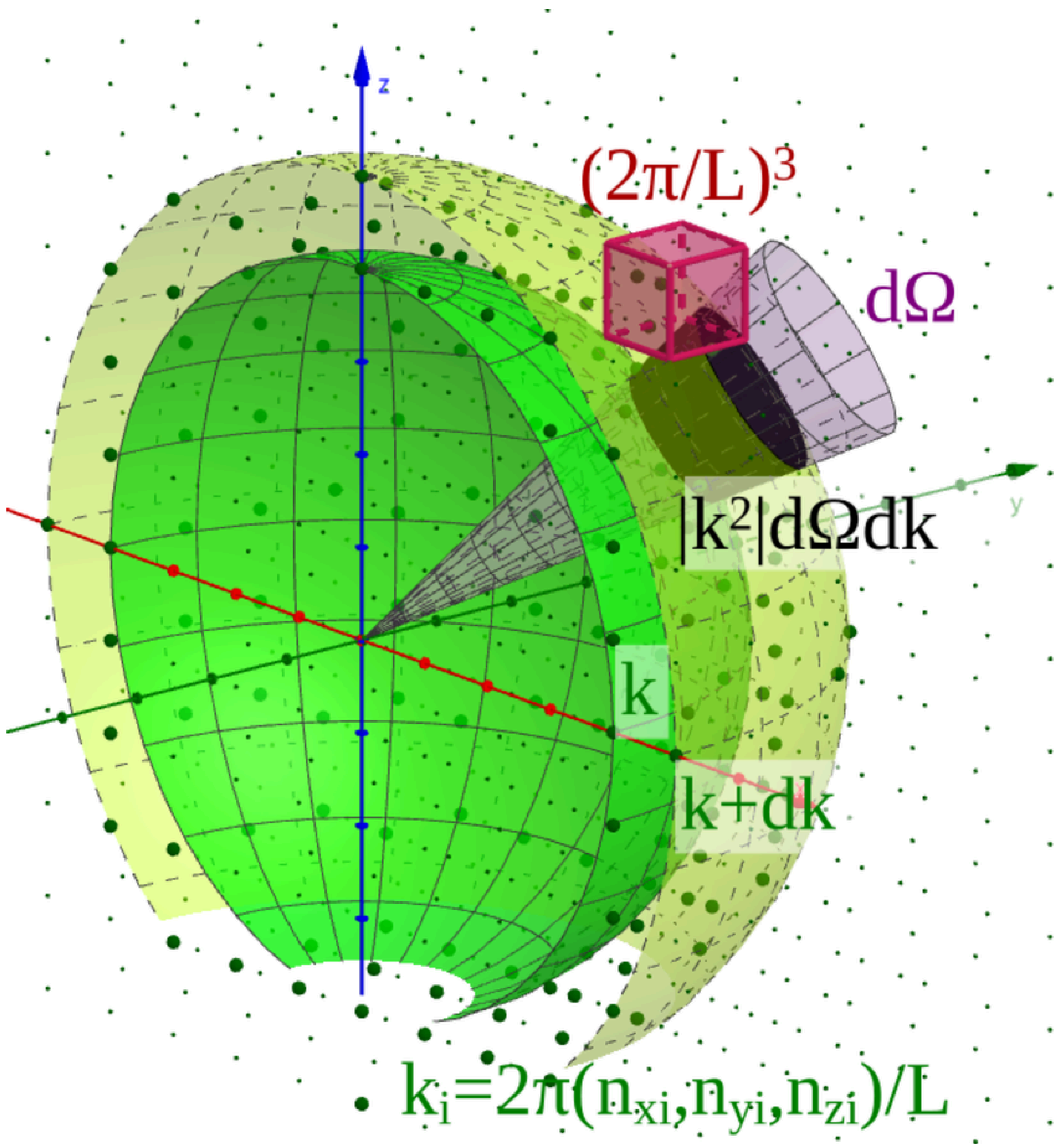



Single-excited valence state
Intermediate state
27: RAS3 - 1 electron
27: RAS1 - 1 hole
100: Inactive - only double occupied orbitals
Sulfur 1s orbital
27: RAS3
126: Inactive
1: RAS1



$$\frac{dP_\mathrm{r}}{d\Omega d\omega} = \frac{dN_{[\omega;\omega+d\omega],d\Omega}}{d\Omega d\omega} \cdot \langle P_\mathrm{m}(\mathbf{k})\rangle_{\text{black volume}} = \frac{L^3}{(2\pi c)^3}\omega^2 P_\mathrm{m}(\mathbf{k})$$