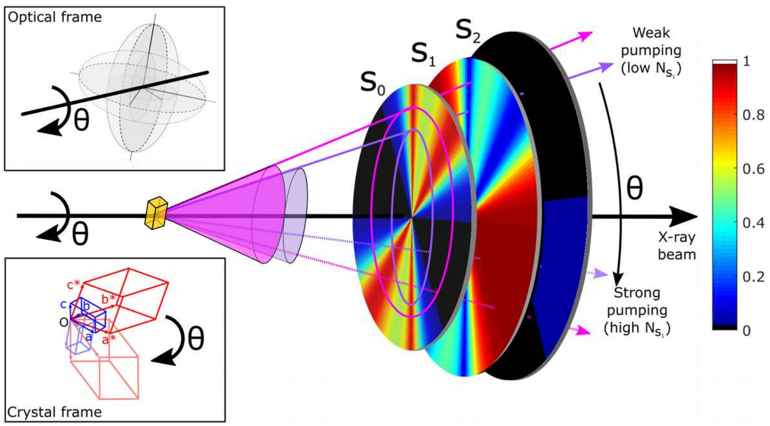
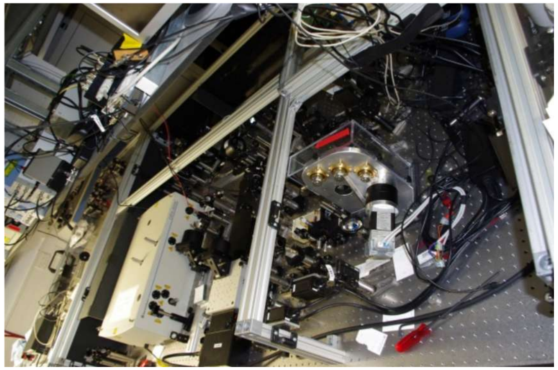
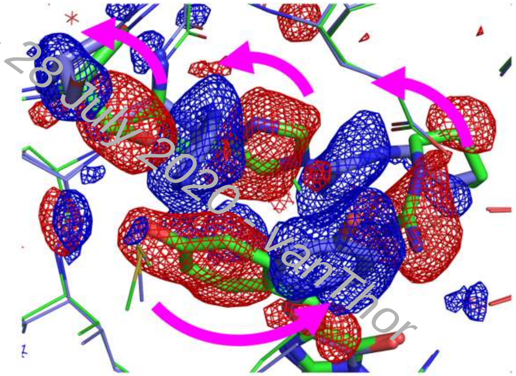
Imperial College London
Jasper van Thor

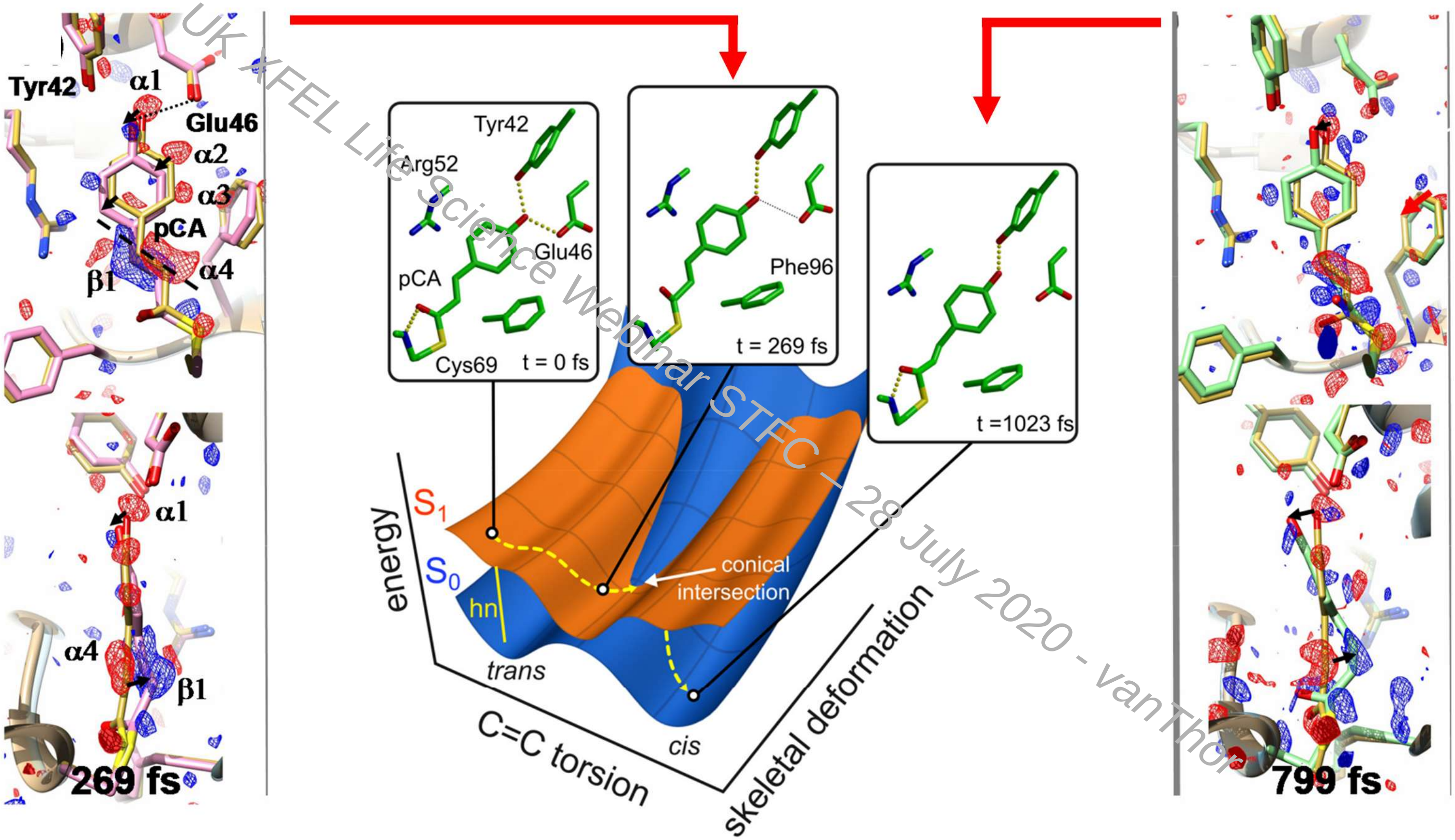
Opportunities in femtosecond time resolved protein crystallography





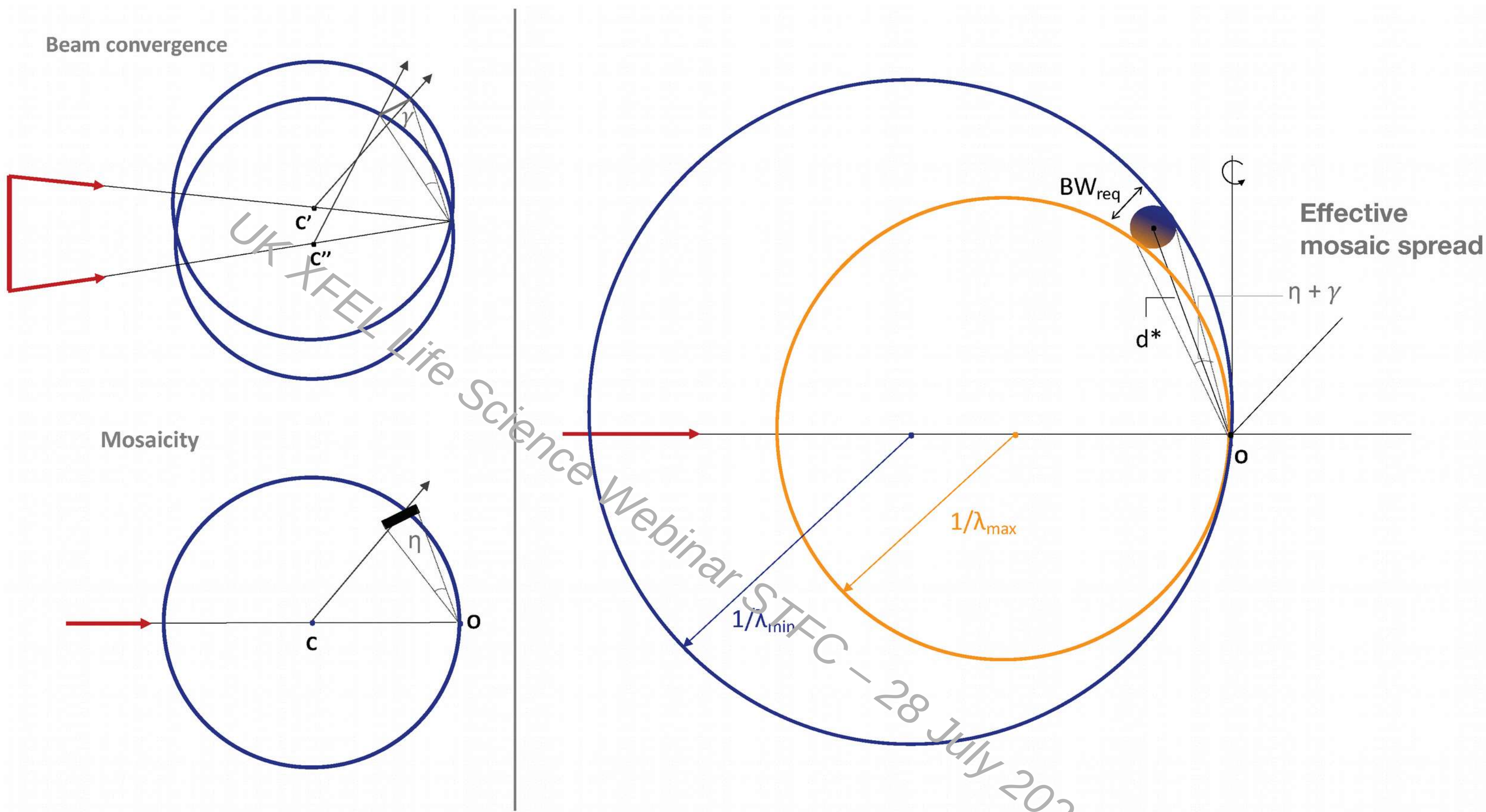


A structural view of ultrafast reaction dynamics



Control of FEL radiation

Possibility for *energy-chirped* ultrafast time resolved diffraction: Exploiting time-to-energy mapping of shaped XFEL pulses



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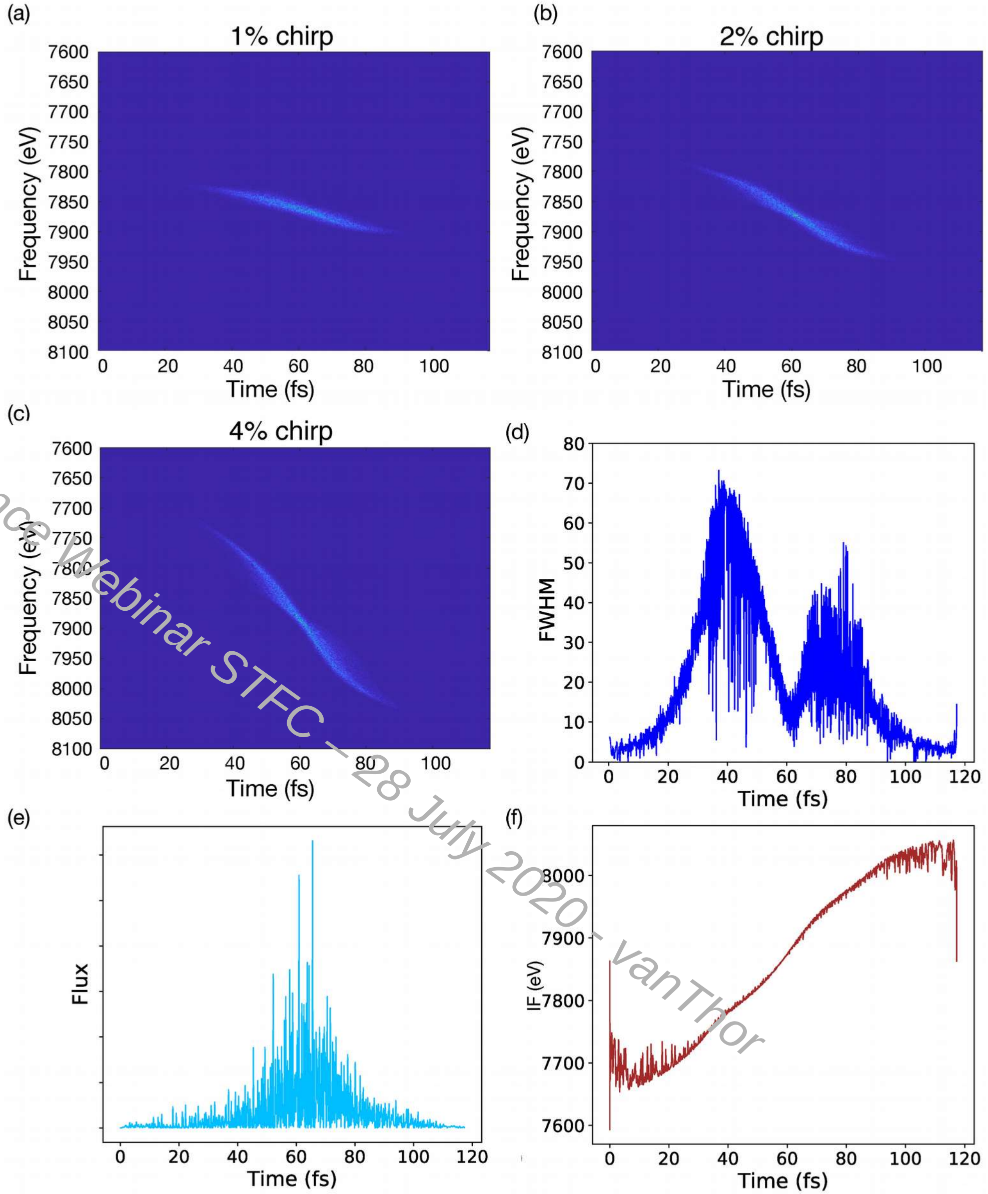
Effect of beam convergence (γ) and mosaicity (η) on the reflection bandwidth (BW req).
BW req depends on the sum of γ and η and on the distance of the reciprocal lattice point from the reciprocal space origin (d*). The minimum (λ min) and maximum (λ max) wavelengths of the spot bandwidth are shown together with the energy gradient across the reflection.

Possibility for *energy-chirped* ultrafast time resolved diffraction: Exploiting time-to-energy mapping of shaped XFEL pulses

Simulations for SwissFEL chirped polychromatic mode

Also now experimentally shown



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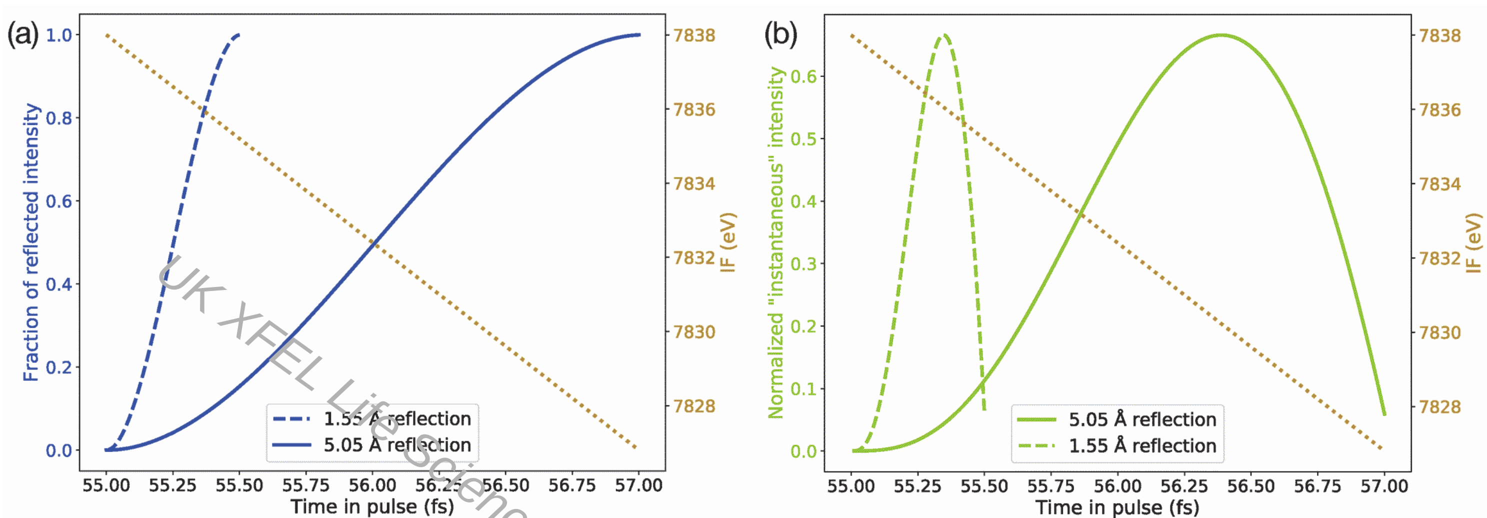
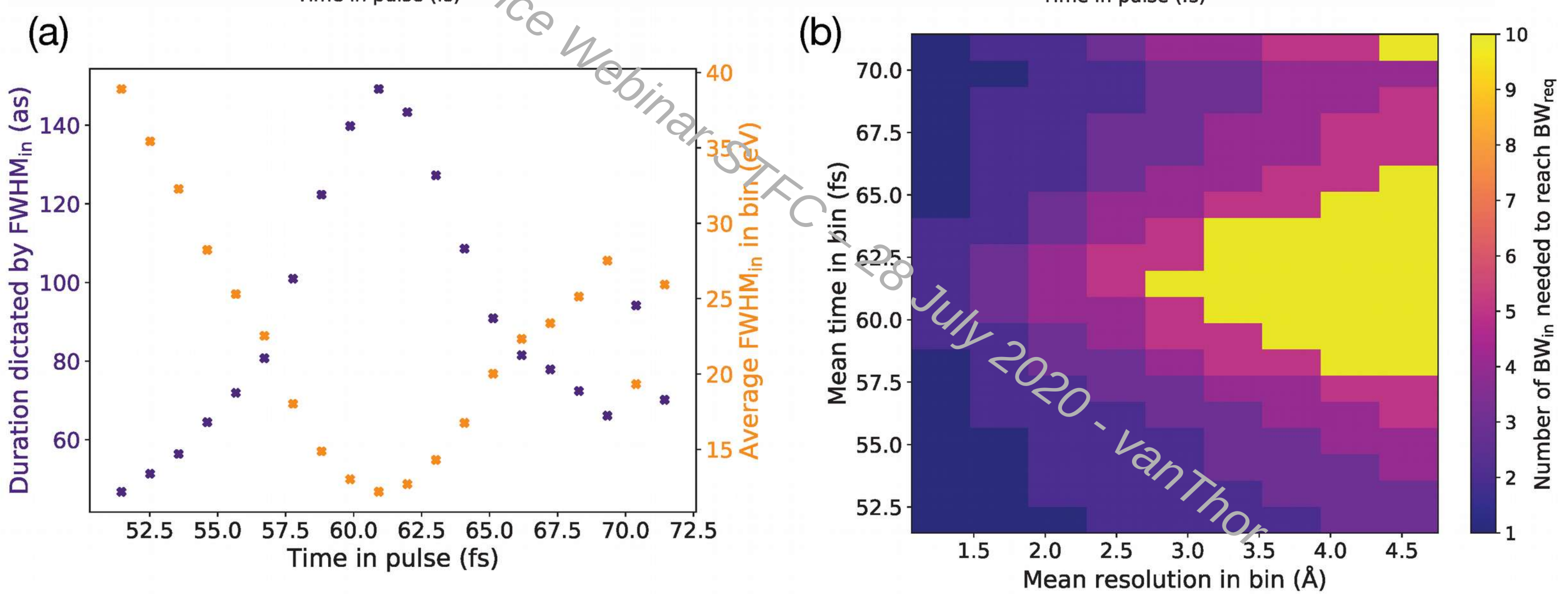
Possibility for *energy-chirped* ultrafast time resolved diffraction: Exploiting time-to-energy mapping of shaped XFEL pulses





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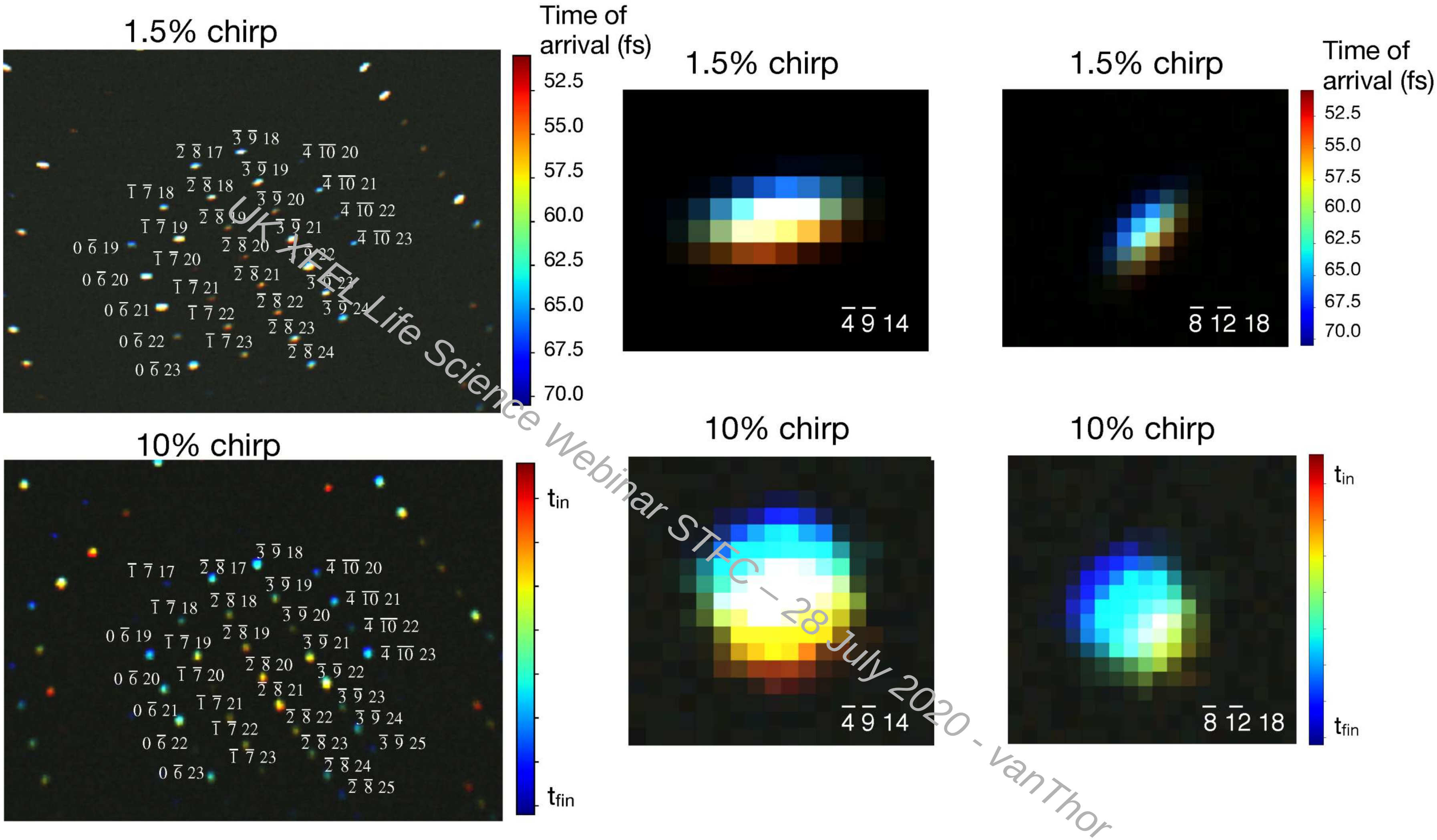
Possibility for *energy-chirped* ultrafast time resolved diffraction: Exploiting time-to-energy mapping of shaped XFEL pulses



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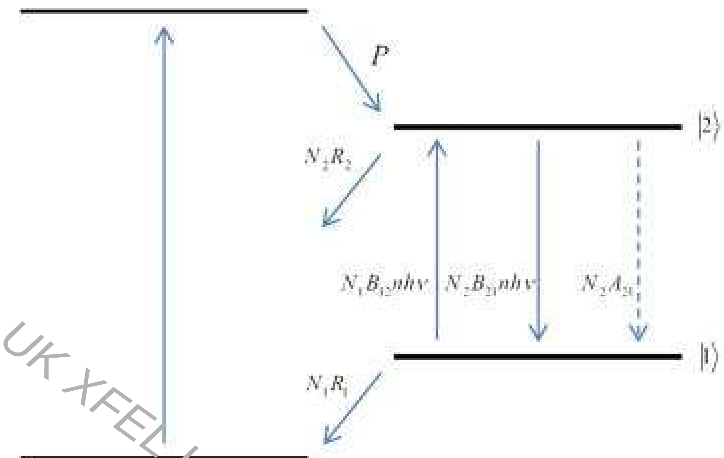
Ultrafast population dynamics analysis:

Exploiting signal-to-noise development

A) Laser rate equations for a 4-level system

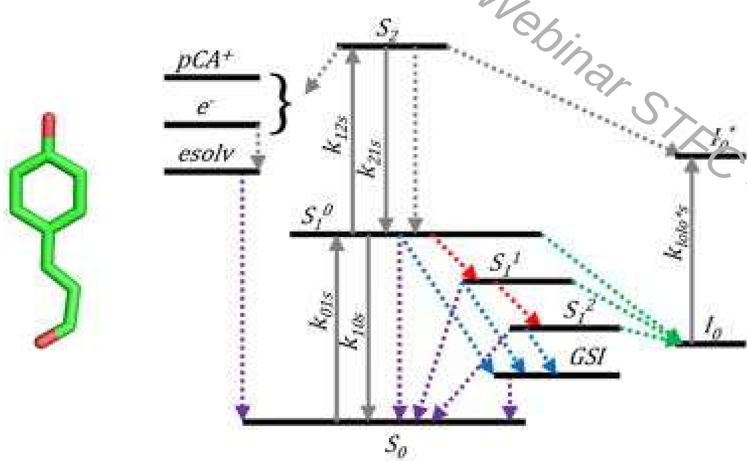


$$\frac{dN_1}{dt} = (N_2 - N_1)B_{21}nh\nu + N_2A_{21} - N_1R_1$$

$$\frac{dN_2}{dt} = P - (N_2 - N_1)B_{21}nh\nu - N_2A_{21} - N_2R$$

$$\frac{dn}{dt} = -\beta n + (N_2 - N_1)B_{21}nh\nu$$

B) Rate equations for a photochemical model for PYP



$$\frac{d[S_1^0]}{dt} = \boldsymbol{k}_{01s}(t)[S_0] - \boldsymbol{k}_{10s}(t)[S_1^0] - \boldsymbol{k}_{12s}(t)[S_1^0] + \boldsymbol{k}_{21s}(t)[S_2] - \varphi_{S_1^0\to S_1^1}\boldsymbol{k}_{S_1^0}[S_1^0] - \varphi_{S_1^0\to I_0}\boldsymbol{k}_{S_1^0}[S_1^0] - \varphi_{S_1^0\to S_{GSI}}\boldsymbol{k}_{S_1^0}[S_1^0] - \varphi_{S_1^0\to S_0}\boldsymbol{k}_{S_1^0}[S_1^0]$$

$$\frac{d[S_1^1]}{dt} = \varphi_{S_1^0\to S_1^1}\boldsymbol{k}_{S_1^0}[S_1^0] - \varphi_{S_1^1\to S_1^2}\boldsymbol{k}_{S_1^1}[S_1^1] - \varphi_{S_1^1\to I_0}\boldsymbol{k}_{S_1^1}[S_1^1] - \varphi_{S_1^1\to S_{GSI}}\boldsymbol{k}_{S_1^1}[S_1^1] - \varphi_{S_1^1\to S_0}\boldsymbol{k}_{S_1^1}[S_1^1]$$

$$\frac{d[S_1^2]}{dt} = \varphi_{S_1^1\to S_1^2}\boldsymbol{k}_{S_1^1}[S_1^1] - \varphi_{S_1^2\to I_0}\boldsymbol{k}_{S_1^2}[S_1^2] - \varphi_{S_1^2\to S_{GSI}}\boldsymbol{k}_{S_1^2}[S_1^2] - \varphi_{S_1^2\to S_0}\boldsymbol{k}_{S_1^2}[S_1^2]$$

$$\frac{d[I_0]}{dt} = \varphi_{S_1^0\to I_0}\boldsymbol{k}_{S_1^0}[S_1^0] + \varphi_{S_1^1\to I_0}\boldsymbol{k}_{S_1^1}[S_1^1] + \varphi_{S_1^2\to I_0}\boldsymbol{k}_{S_1^2}[S_1^2] - \boldsymbol{k}_{I_0}[I_0]$$

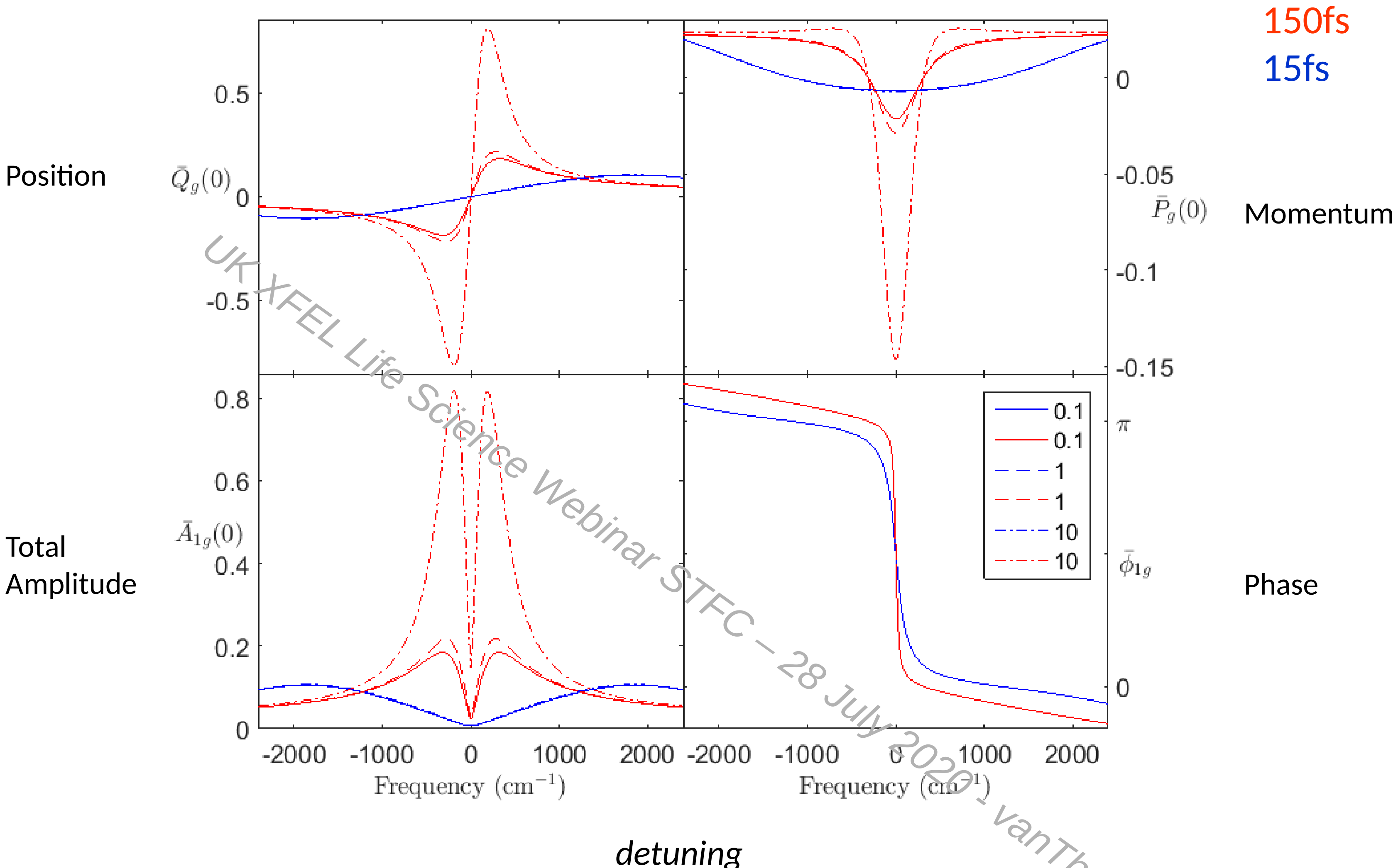
$$\frac{d[S_{GSI}]}{dt} = \varphi_{S_1^0\to S_{GSI}}\boldsymbol{k}_{S_1^0}[S_1^0] + \varphi_{S_1^1\to S_{GSI}}\boldsymbol{k}_{S_1^1}[S_1^1] + \varphi_{S_1^2\to S_{GSI}}\boldsymbol{k}_{S_1^2}[S_1^2] - \boldsymbol{k}_{S_{GSI}}[S_{GSI}]$$

$$\frac{d[S_2]}{dt} = \boldsymbol{k}_{12s}(t)[S_1^0] - \boldsymbol{k}_{21s}(t)[S_2] - \varphi_{S_2\to e^-}\boldsymbol{k}_{S_2}[S_2] - \varphi_{S_2\to S_0}\boldsymbol{k}_{S_2}[S_2]$$

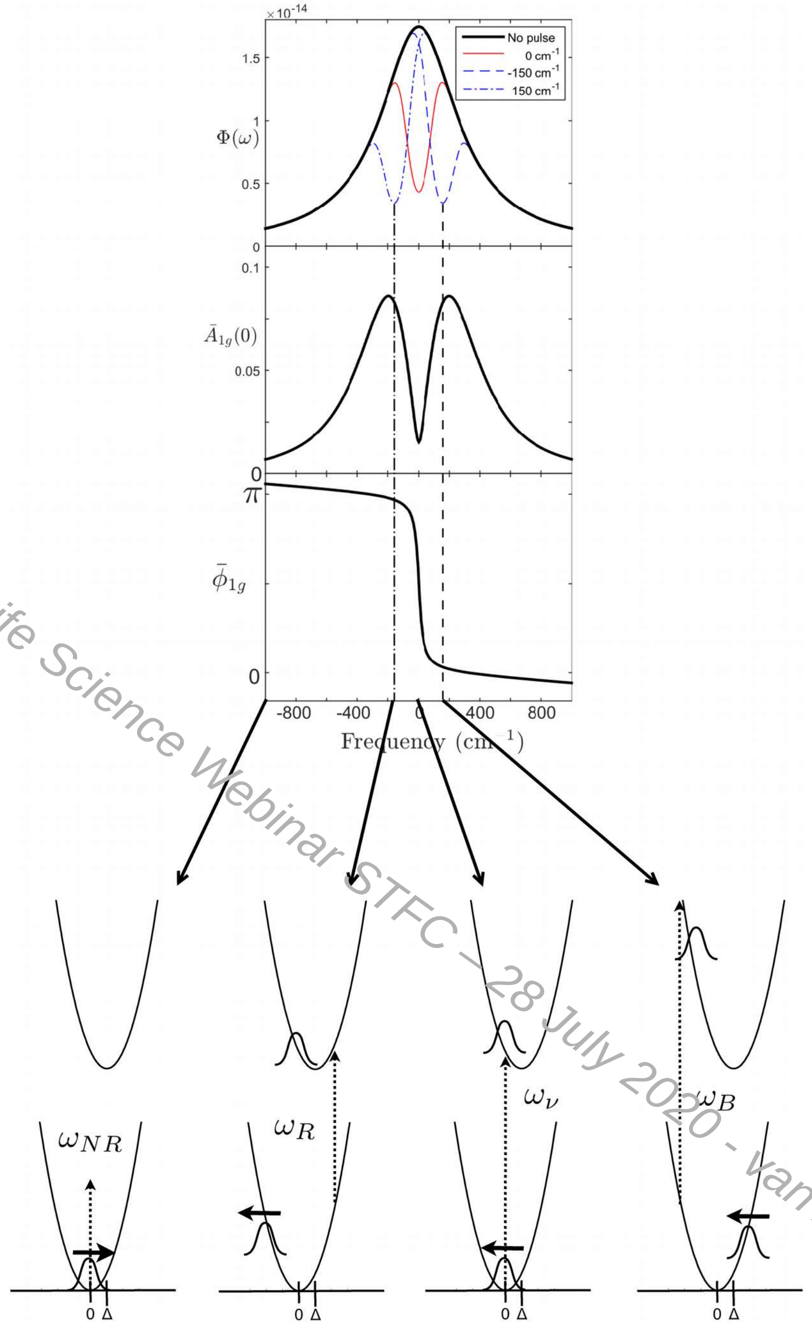
$$\frac{d[e^-]}{dt} = \varphi_{S_2\to e^-}\boldsymbol{k}_{S_2}[S_2]$$

van Thor, J.J. Structural Dynamics 6, 050901 (2019)

Linear response theory estimates the magnitude of ground state coherence



Hutchison and van Thor (2017) Populations and coherence in femtosecond time resolved X-ray crystallography of the photoactive yellow protein. ***Int.Rev.Phys.Chem. 36***; 117



van Thor, J.J. Structural Dynamics 6, 050901 (2019)

The consequences of crystal optics

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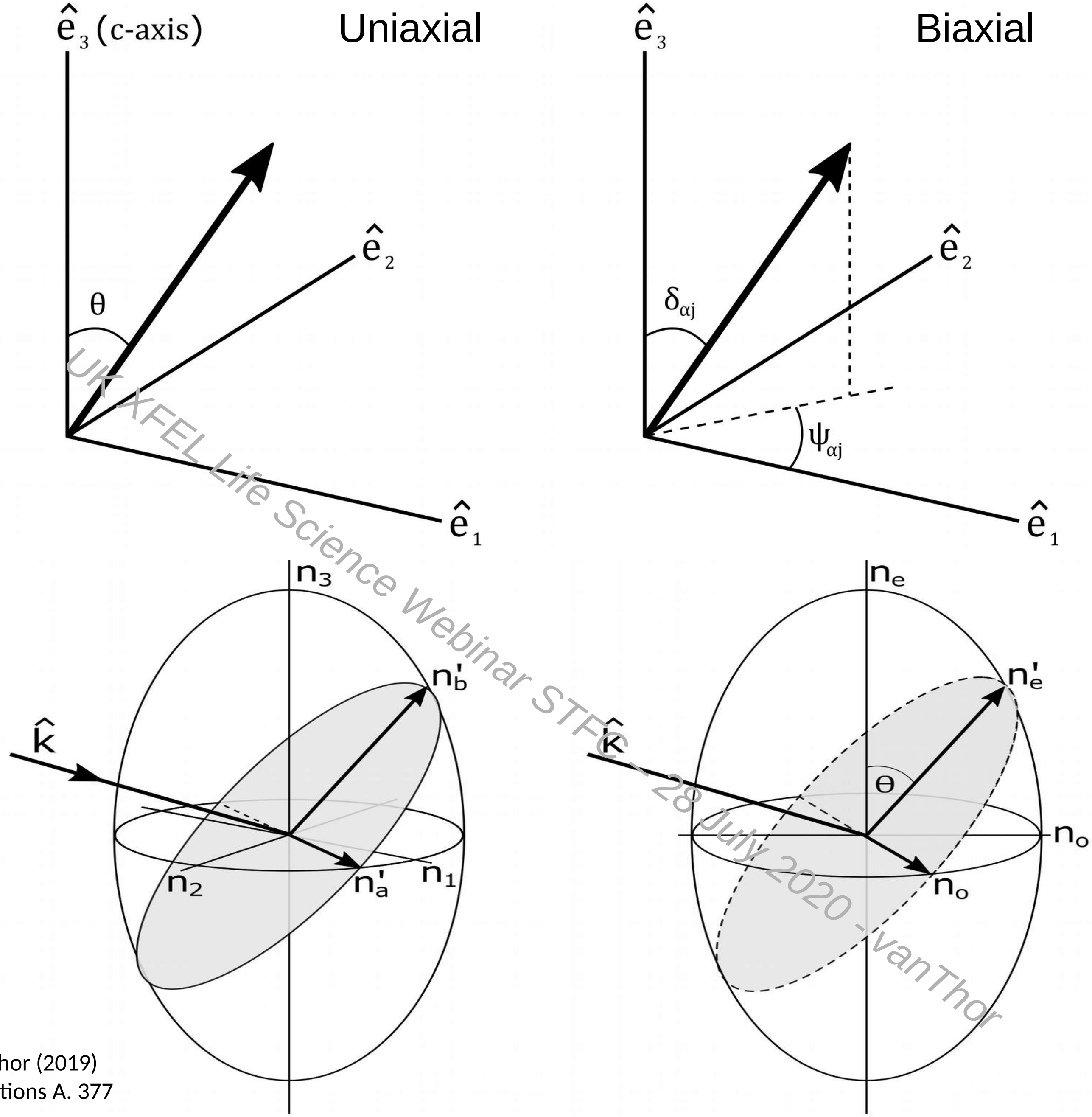
populations and coherence



Hutchison and van Thor (2019)
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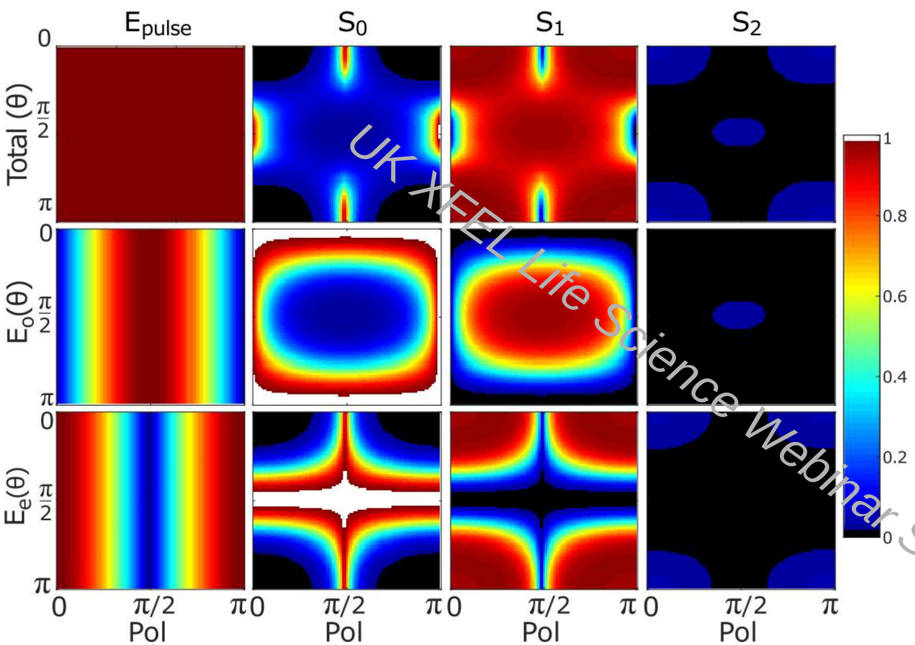
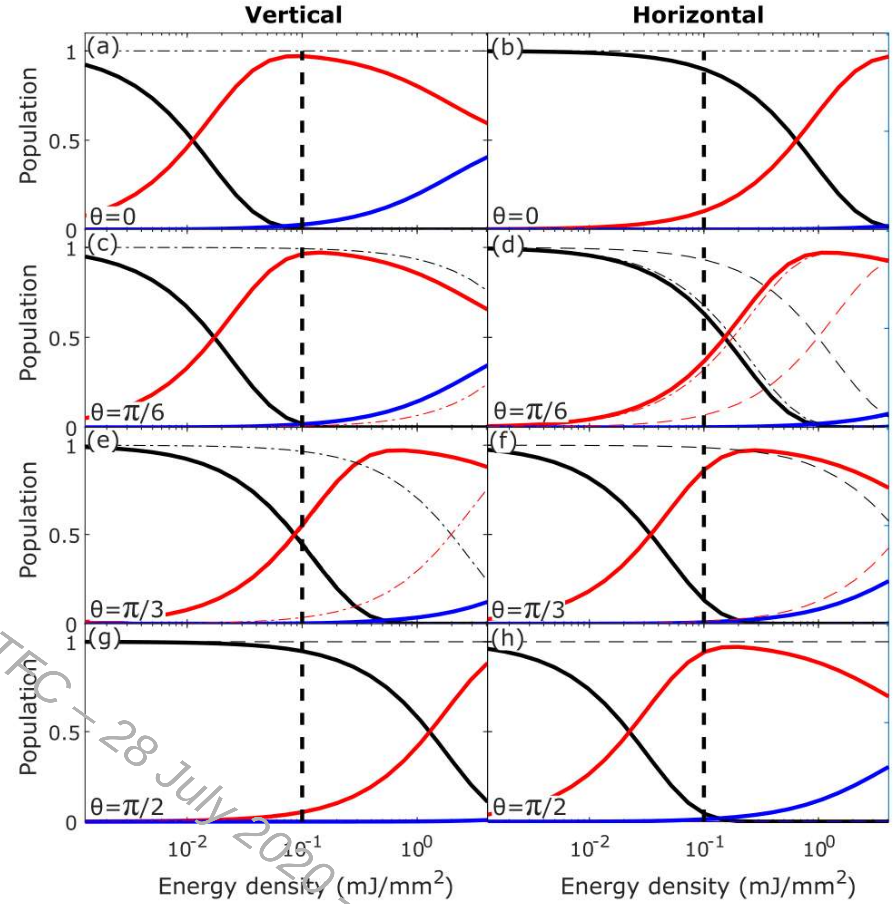
For each orientation a linear combination of two fields prepares the populations





Hutchison and van Thor (2019)
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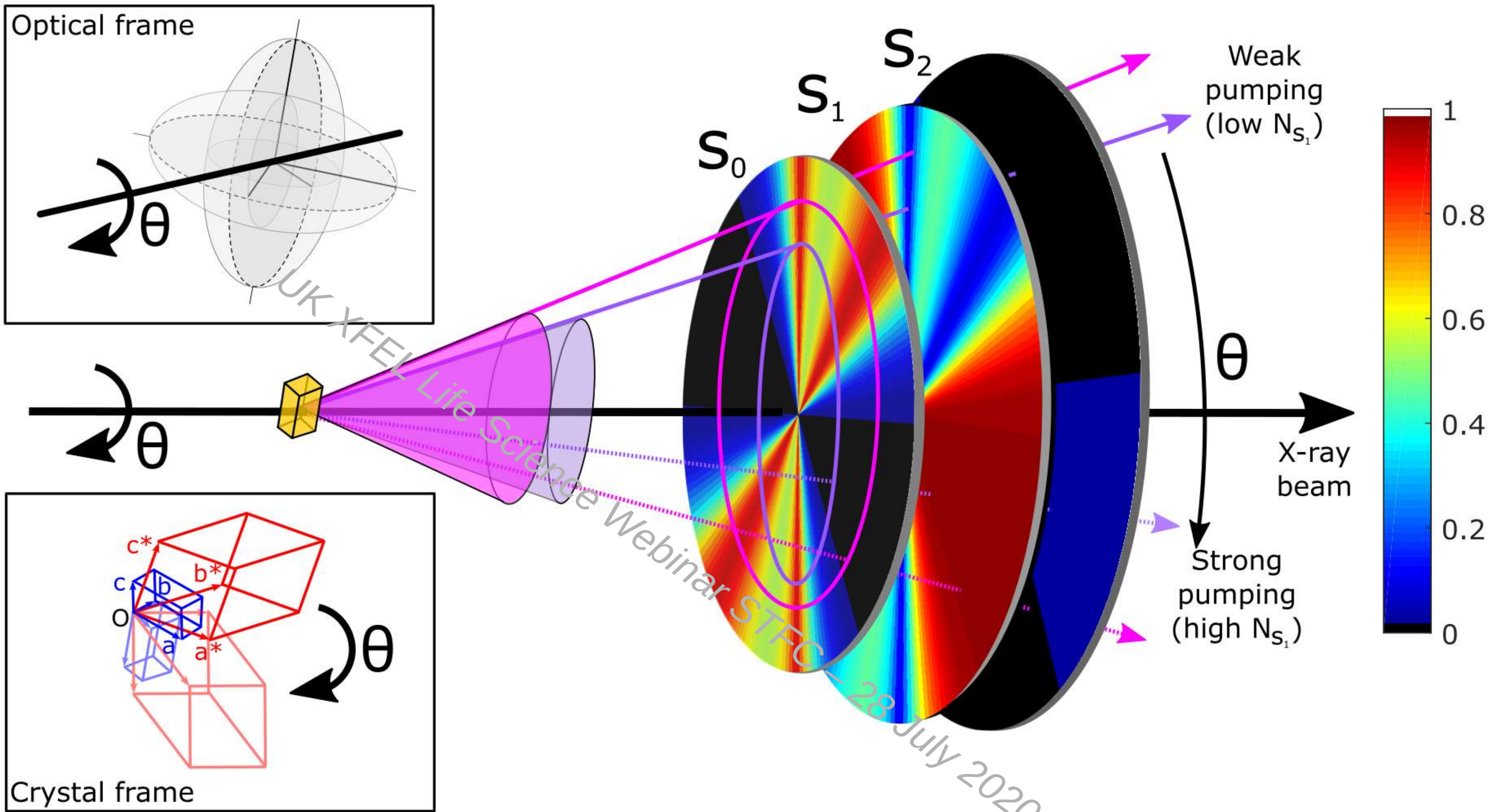

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The real-space relationship to the third order response

Uniaxial example

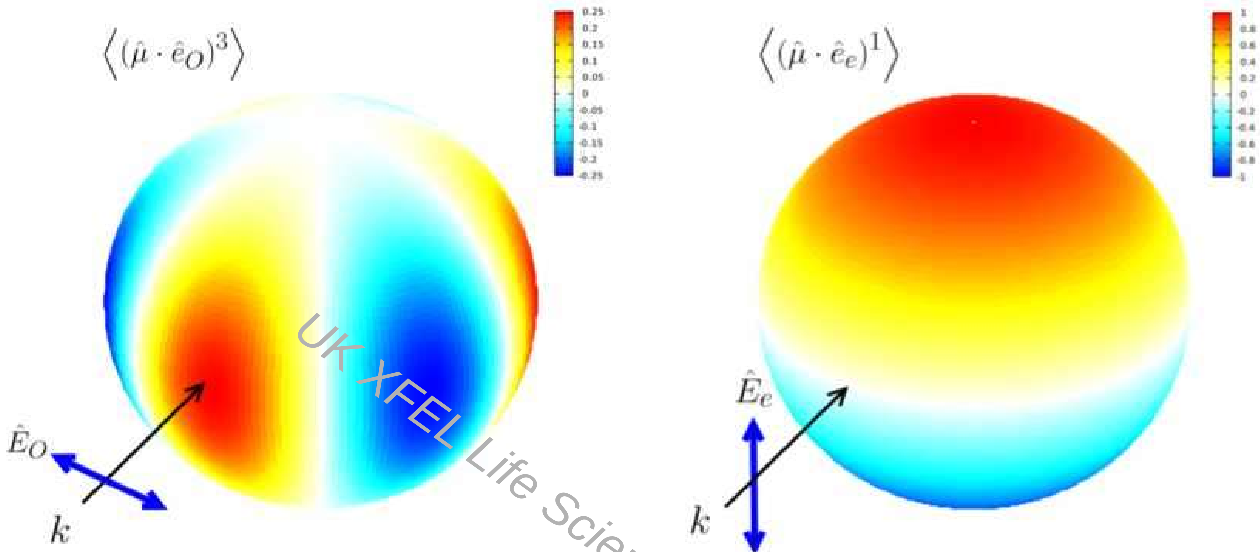


FIG. 5. A real-space plot of the third order response of an isolated oscillator with combination of three interactions in the ordinary directions (left) and a single interaction in the extraordinary direction (right) in the presence of trigonal symmetry, corresponding to a dipole-allowed ⟨OOOE⟩ interaction.

General biaxial case

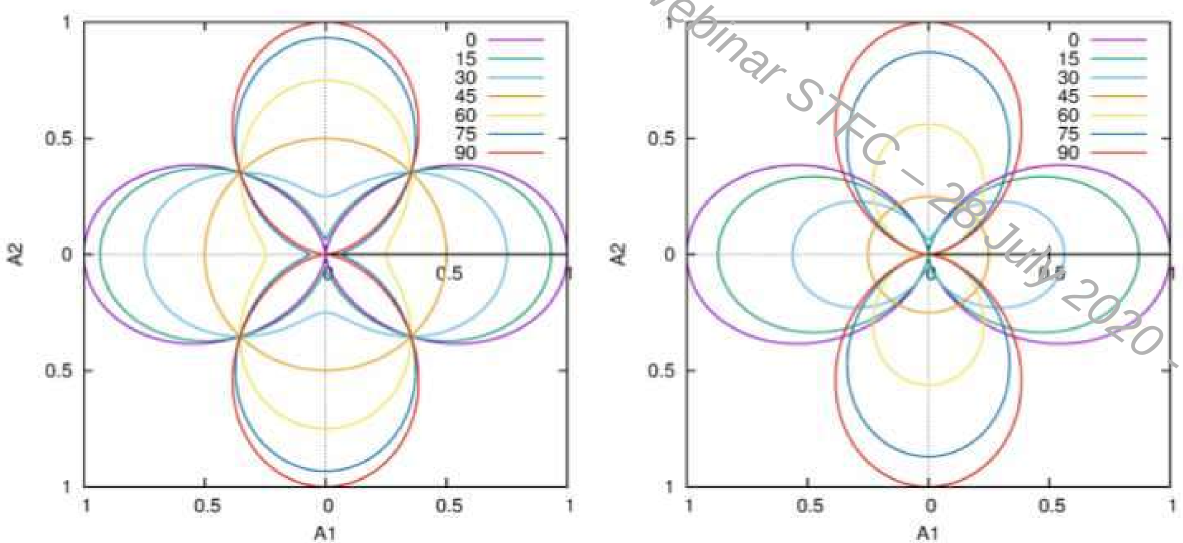
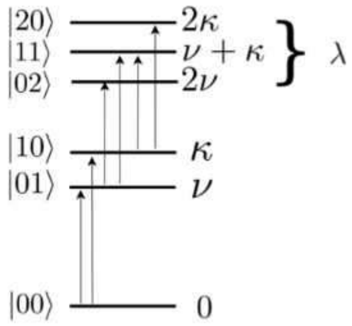
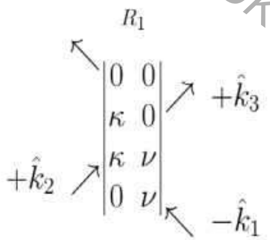


FIG. 6. The general case for the second rank (left) and fourth rank (right) dipole allowed response for an isolated oscillator in biaxial crystals, with k orthogonal to the e3-e2 plane. The components in two orthogonal dielectric axes (labelled here A1 and A2) are plotted for values of Ψ in the geometry shown in Fig. 3 with a direction k.

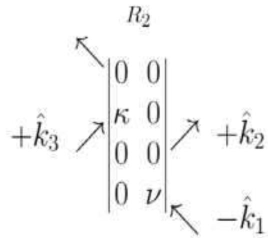
J.J. van Thor (2019) J. Chem. Phys. 21:1224-1234
J.J. van Thor,(2019). Structural Dynamics 6, 050901



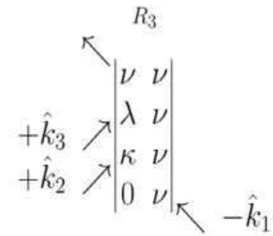
Response function formalism for coupled oscillators



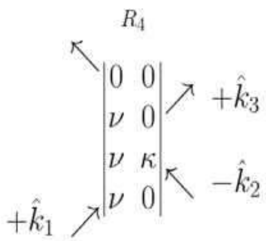
$$\left\langle \left(\hat{\mu}_{0\nu}\cdot\hat{E}_1\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_2\right)\left(\hat{\mu}_{0\nu}\cdot\hat{E}_3\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_4\right)\right\rangle$$



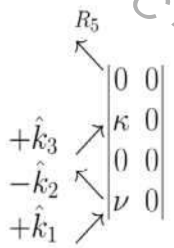
$$\left\langle \left(\hat{\mu}_{0\nu}\cdot\hat{E}_1\right)\left(\hat{\mu}_{0\nu}\cdot\hat{E}_2\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_3\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_4\right)\right\rangle$$



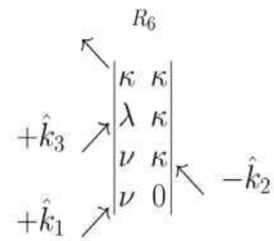
$$\left\langle \left(\hat{\mu}_{0\nu}\cdot\hat{E}_1\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_2\right)\left(\hat{\mu}_{\kappa\lambda}\cdot\hat{E}_3\right)\left(\hat{\mu}_{\lambda\nu}\cdot\hat{E}_4\right)\right\rangle$$



$$\left\langle \left(\hat{\mu}_{0\nu}\cdot\hat{E}_1\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_2\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_3\right)\left(\hat{\mu}_{0\nu}\cdot\hat{E}_4\right)\right\rangle$$



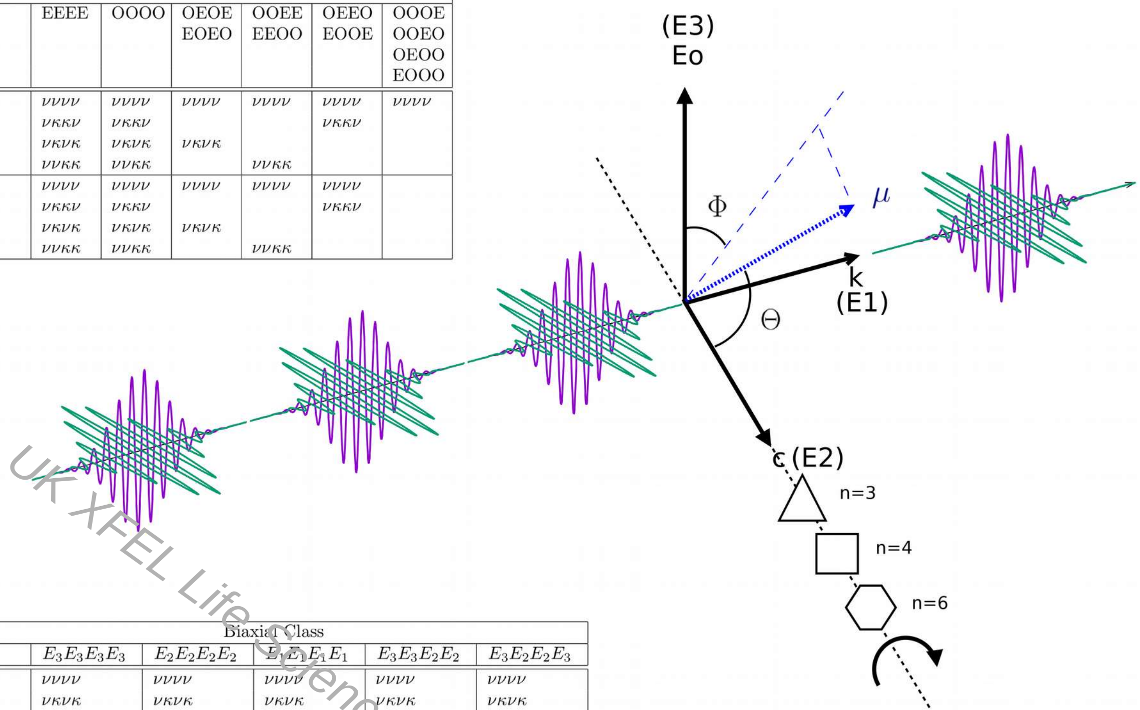
$$\left\langle \left(\hat{\mu}_{0\nu}\cdot\hat{E}_1\right)\left(\hat{\mu}_{0\nu}\cdot\hat{E}_2\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_3\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_4\right)\right\rangle$$



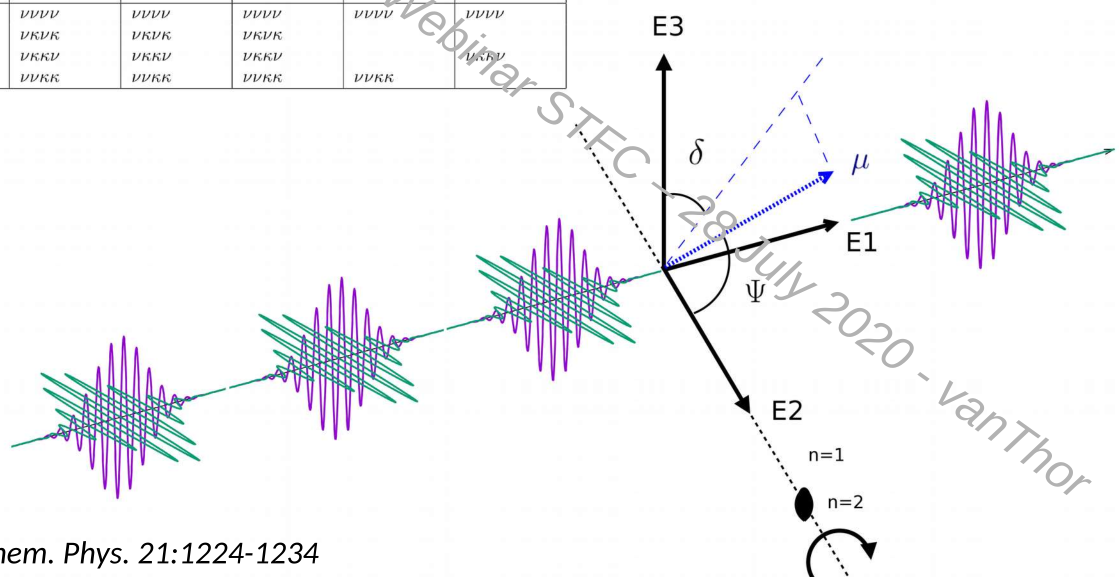
$$\left\langle \left(\hat{\mu}_{0\nu}\cdot\hat{E}_1\right)\left(\hat{\mu}_{0\kappa}\cdot\hat{E}_2\right)\left(\hat{\mu}_{\nu\lambda}\cdot\hat{E}_3\right)\left(\hat{\mu}_{\lambda\kappa}\cdot\hat{E}_4\right)\right\rangle$$

J.J. van Thor (2019) J. Chem. Phys. 21:1224-1234
J.J. van Thor,(2019). Structural Dynamics 6, 050901

Uniaxial Class						
n	EEEE	OOOO	OEOE EOEO	OOEE EEOO	OEEO EOOE	OOOE OOEO OEOO EOOO
3	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$ $\nu\kappa\nu\kappa$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$ $\nu\kappa\nu\kappa$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$	$\nu\nu\nu\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$	$\nu\nu\nu\nu$
4,6	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$ $\nu\kappa\nu\kappa$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$ $\nu\kappa\nu\kappa$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$	$\nu\nu\nu\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$	



Biaxial Class					
n	$E_3E_3E_3E_3$	$E_2E_2E_2E_2$	$E_1E_1E_1E_1$	$E_3E_3E_2E_2$	$E_3E_2E_2E_3$
1	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$
2	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\nu\kappa$ $\nu\kappa\kappa\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\nu\kappa\kappa$	$\nu\nu\nu\nu$ $\nu\kappa\kappa\nu$



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