

Core-level photoexcitation of metals by
intense x-ray free-electron laser (XFEL):
Quantum kinetics and nonlinear photonics

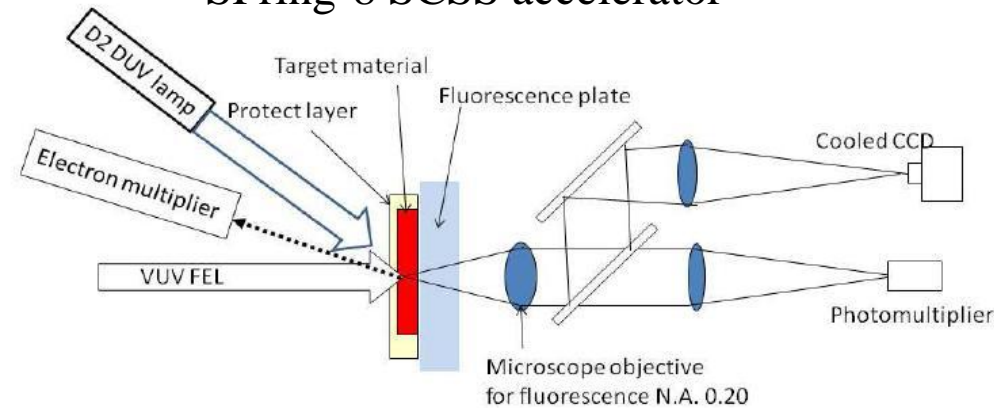
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Nonlinear transmission of VUV FEL pulse through Sn

H. Yoneda *et al.*, Opt. Express **17**, 23443 (2009)

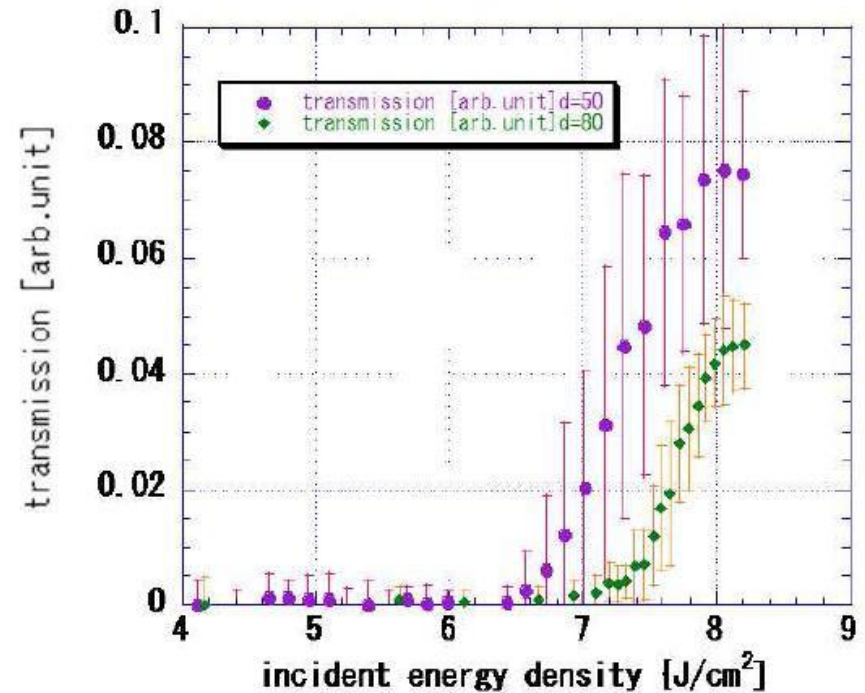
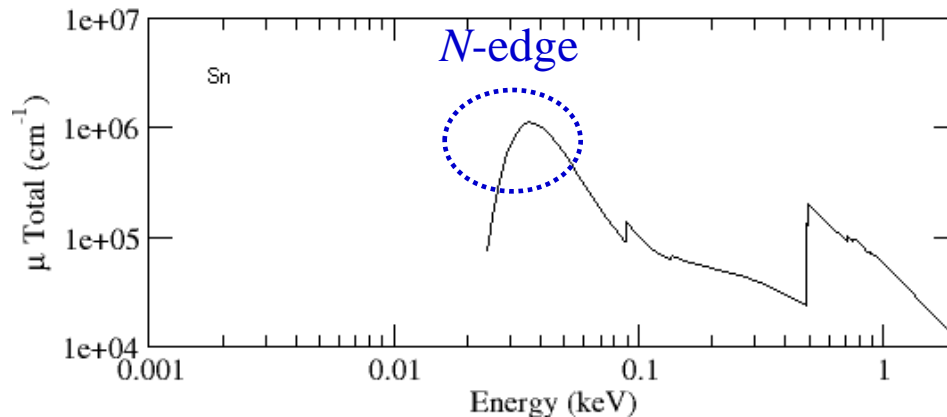
SPring-8 SCSS accelerator



Sn target (50-80 nm thickness)

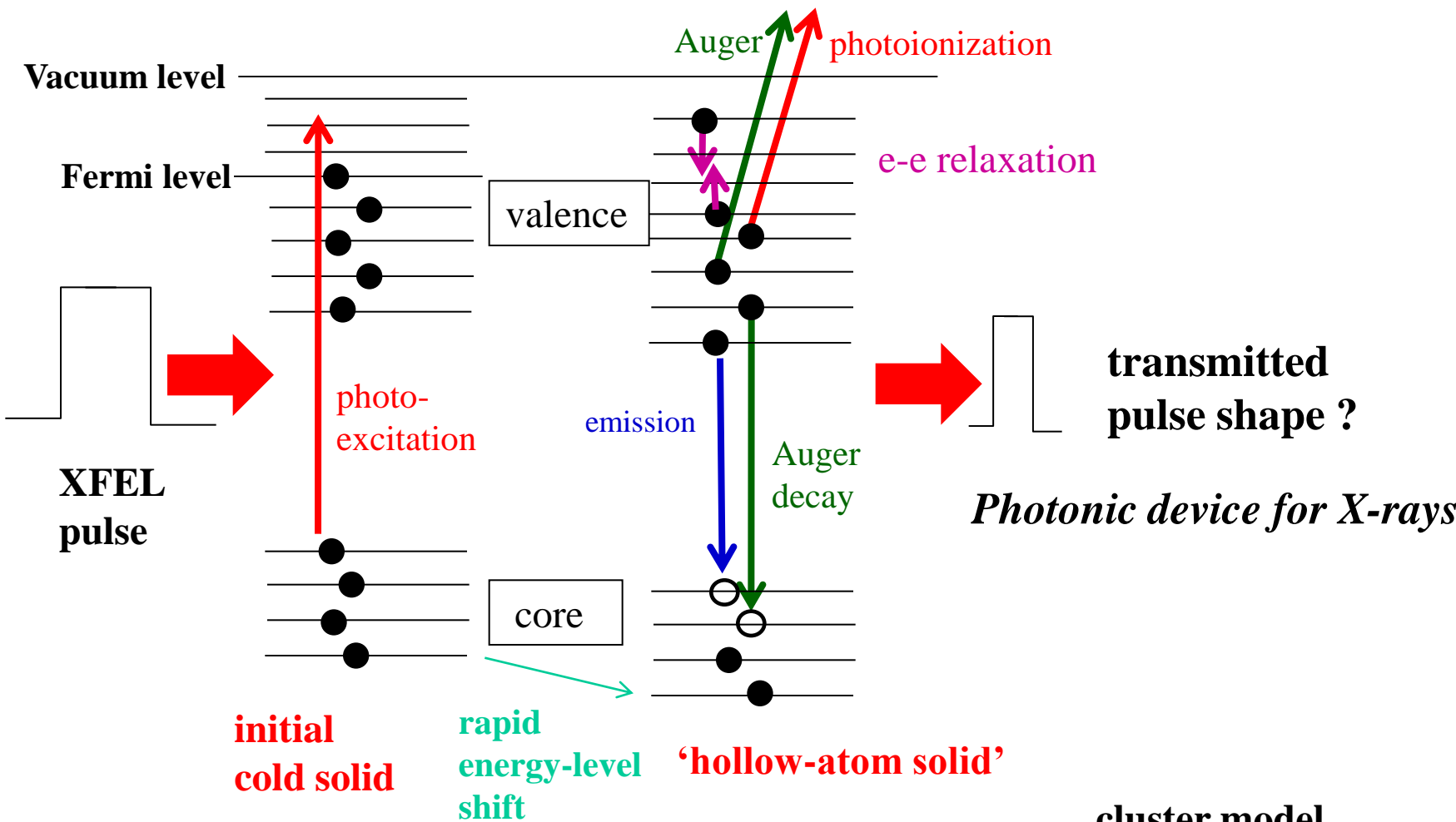
$$\hbar\omega_{\nu} = 20\text{-}25 \text{ eV}$$

$$\Delta t = 100 \text{ fs}$$



Saturable absorption in VUV range

Simulation of elementary processes in highly core-excited metals

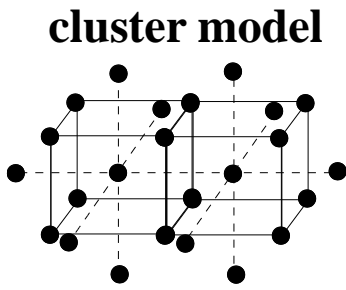


molecular orbitals (MOs)

$$\psi_k^\sigma(\mathbf{r}) = \sum_{\mu=1}^N \sum_{i=1}^{N_{\text{STO}}} c_{k,i\mu}^\sigma \phi_i(\mathbf{r} - \mathbf{R}_\mu)$$

Slater-type atomic orbital

$\sigma = \alpha$ (up spin)
 $\sigma = \beta$ (down spin)



Total Hamiltonian

MO energy levels (unrestricted Hartree-Fock calculation)

$$\begin{aligned}
 H = & \sum_{k\sigma} \overset{\downarrow}{\epsilon_k^\sigma} c_{k\sigma}^\dagger c_{k\sigma} - \sum_{k_1 k_2 \sigma} \sum_{k_3 \sigma'}^{\text{occ}} \left(V_{k_1 k_2 k_3 k_3}^{\sigma\sigma'} - \delta_{\sigma\sigma'} V_{k_1 k_2 k_3 k_3}^{\sigma\sigma'} \right) c_{k_1 \sigma}^\dagger c_{k_2 \sigma} \\
 & + \frac{1}{2} \sum_{\substack{k_1 k_2 k_3 k_4 \\ \sigma\sigma'}} V_{k_1 k_2 k_3 k_4}^{\sigma\sigma'} c_{k_1 \sigma}^\dagger c_{k_3 \sigma'}^\dagger c_{k_4 \sigma'} c_{k_2 \sigma} + \frac{e}{m_e c} \mathbf{A}(t) \cdot \sum_{k_1 k_2 \sigma} \mathbf{p}_{k_1 k_2}^\sigma c_{k_1 \sigma}^\dagger c_{k_2 \sigma}
 \end{aligned}$$

electron-electron interaction
electron-photon interaction

$$\delta_{k_1 \sigma_1}^{\text{occ}} \equiv \begin{cases} 1 & \text{if state } (k_1, \sigma_1) \text{ is occupied in the ground state} \\ 0 & \text{otherwise} \end{cases}$$

$$V_{k_1 k_2 k_3 k_4}^{\sigma_1 \sigma_2} \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_{k_1}^{\sigma_1*}(\mathbf{r}_1) \psi_{k_2}^{\sigma_1}(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{k_3}^{\sigma_2*}(\mathbf{r}_2) \psi_{k_4}^{\sigma_2}(\mathbf{r}_2)$$

$$\mathbf{p}_{k_1 k_2}^\sigma \equiv \int d\mathbf{r} \psi_{k_1}^{\sigma*}(\mathbf{r}) \frac{\hbar}{i} \nabla \psi_{k_2}^\sigma(\mathbf{r}) \quad \text{momentum operator}$$

$$\mathbf{A}(t) = \frac{1}{2} \mathbf{A}_0 \exp(-i\omega_\nu t) + \text{cc} \quad \text{vector potential of the laser field}$$

Density matrix equation for electron dynamics

$\rho_{kk'\sigma} \equiv c_{k\sigma}^\dagger c_{k'\sigma}$ operator of density-fluctuation excitation

$\langle \rho_{kk'\sigma} \rangle$: one-particle density matrix $\langle \dots \rangle$: expectation value

$$i\hbar \frac{\partial}{\partial t} \langle \rho_{kk'\sigma}(t) \rangle = \left\langle \left[c_{k\sigma}^\dagger c_{k'\sigma}, H(t) \right] \right\rangle \quad \text{equation of motion}$$

$f_{k\sigma}(t) \equiv \langle \rho_{kk\sigma}(t) \rangle$ diagonal element = population of k th MO

$K_{kk_3k_1k_2}^{\sigma\sigma_1} \equiv \langle c_{k\sigma}^\dagger c_{k_1\sigma_1}^\dagger c_{k_2\sigma_1} c_{k_3\sigma} \rangle$ two-particle density matrix

$$\equiv \underbrace{\langle \rho_{kk_3\sigma} \rangle \langle \rho_{k_1k_2\sigma_1} \rangle - \delta_{\sigma\sigma_1} \langle \rho_{k_1k_3\sigma} \rangle \langle \rho_{kk_2\sigma} \rangle}_{\text{H-F}} + \delta K_{kk_3k_1k_2}^{\sigma\sigma_1} \quad \text{correlation}$$

Born approximation + exchange

$$i\hbar \frac{\partial \delta K_{kk_3k_1k_2}^{\sigma\sigma_1}(t)}{\partial t} = \left[\tilde{\varepsilon}_{k_3\sigma}(t) + \tilde{\varepsilon}_{k_2\sigma_1}(t) - \tilde{\varepsilon}_{k_1\sigma_1}(t) - \tilde{\varepsilon}_{k\sigma}(t) \right] \delta K_{kk_3k_1k_2}^{\sigma\sigma_1}(t) + S_{kk_3k_1k_2}^{\sigma\sigma_1}(t)$$

Effects of electron-hole interaction

$$\tilde{\varepsilon}_{kk'\sigma}(t) \equiv \sum_{k_1 k_2 \sigma_1} \left(V_{kk'k_1 k_2}^{\sigma\sigma_1} - \delta_{\sigma\sigma_1} V_{kk_2 k_1 k'}^{\sigma\sigma} \right) \left[\langle \rho_{k_1 k_2 \sigma}(t) \rangle - \delta_{k_1 k_2} \delta_{k_1 \sigma_1}^{\text{occ}} \right] \quad \text{self-energy matrix}$$

$$V_{kk_3 k_1 k_2}^{\sigma\sigma_1} \approx \begin{cases} \sum_{ij\mu} \sum_{i'j'\mu'} c_{k,i\mu}^{\sigma*} c_{k_3,j\mu}^{\sigma} c_{k_1,i'\mu'}^{\sigma_1*} c_{k_2,j'\mu'}^{\sigma_1} (i\mu, j\mu | i'\mu', j'\mu') , & \text{for } |\mathbf{R}_\mu - \mathbf{R}_{\mu'}| \leq R_{\text{nn}} \\ 0, & \text{otherwise} \end{cases}$$

cutoff at nearest-neighbor separation
→ screening effect

(1) renormalized energy level

$$\tilde{\varepsilon}_{k\sigma}(t) = \varepsilon_{k\sigma} + \tilde{\varepsilon}_{kk\sigma}(t)$$

shift

(2) renormalized transition energy $k' \rightarrow k$

$$\hbar \tilde{\omega}_{kk'\sigma}^{\text{IVO}}(t) \equiv \tilde{\varepsilon}_{k\sigma}(t) - \tilde{\varepsilon}_{k'\sigma}(t) - \frac{\left(V_{k'k'kk}^{\sigma\sigma} - V_{k'kkk'}^{\sigma\sigma} \right) \left[f_{k'\sigma}(t) - f_{k\sigma}(t) \right]}{\left(e-h \text{ attraction: improved virtual orbital} \right)}$$

(3) renormalized transition matrix in ‘RPA+exchange’

$$\tilde{\mathbf{p}}_{kk'}^{\sigma}(\omega) = \mathbf{p}_{kk'}^{\sigma} + \sum_{\substack{k_1 k_2 \sigma_1 \\ (\neq kk'\sigma)}} \left(V_{kk'k_2 k_1}^{\sigma\sigma_1} - \delta_{\sigma\sigma_1} V_{kk_1 k_2 k'}^{\sigma\sigma_1} \right) \frac{\omega - \tilde{\omega}_{k_1 k_2 \sigma_1}^{\text{IVO}} - i\Gamma}{\left(\omega - \tilde{\omega}_{k_1 k_2 \sigma_1}^{\text{IVO}} \right)^2 + \Gamma^2} \left[f_{k_2 \sigma_1}(t) - f_{k_1 \sigma_1}(t) \right] \frac{\tilde{\mathbf{p}}_{k_1 k_2}^{\sigma_1}(\omega)}{\hbar}$$

Markov approximation



Generalized rate equation

H.K., J. Phys. B **43**, 115601 (2010)

$$\frac{\partial f_{k\sigma}(t)}{\partial t} = \frac{I_\nu}{\hbar\omega_\nu} \left[\sum_{k'(\neq k)} \sigma_{kk'\sigma}(\omega_\nu) [f_{k'\sigma}(t) - f_{k\sigma}(t)] - \sigma_{k\sigma}^{\text{bf}}(\omega_\nu) f_{k\sigma}(t) \right] \begin{array}{l} \text{radiative} \\ \text{(bound-bound,} \\ \text{bound-free)} \end{array}$$
$$+ \left. \frac{\partial f_{k\sigma}(t)}{\partial t} \right]_{\text{coll}} + \left. \frac{\partial f_{k\sigma}(t)}{\partial t} \right]_{\text{Auger}} \quad \begin{array}{l} \text{e-e collision} \\ \text{(intravalence, Auger)} \end{array}$$
$$I_\nu = \frac{\omega_\nu^2 |\mathbf{A}_0|^2}{8\pi c} \quad \text{laser intensity}$$

Assumption: *Continuum population = 0*
(*Escape freely without heating or recombination*)

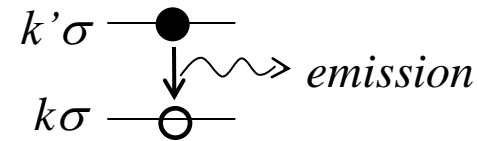
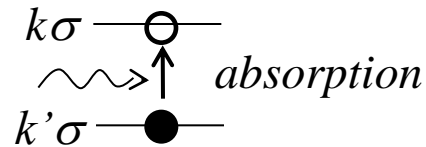
Radiative cross-sections

Bound-bound

averaged over polarization

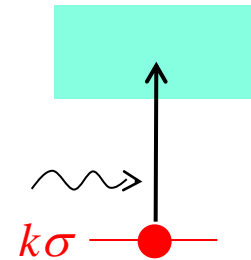
$$\sigma_{kk'\sigma}(\omega) = \frac{4\pi e^2}{c\hbar m_e^2 \omega} \left[\left\langle \left| \tilde{p}_{kk'}^\sigma(\omega) \right|^2 \right\rangle \frac{\Gamma}{(\omega - \tilde{\omega}_{kk'\sigma}^{\text{IVO}}(t))^2 + \Gamma^2} + \left\langle \left| \tilde{p}_{kk'}^\sigma(-\omega) \right|^2 \right\rangle \frac{\Gamma}{(\omega + \tilde{\omega}_{kk'\sigma}^{\text{IVO}}(t))^2 + \Gamma^2} \right]$$

$$= \sigma_{kk'\sigma}^{\text{abs}}(\omega) + \sigma_{kk'\sigma}^{\text{emi}}(\omega)$$



Bound-free

$$\sigma_{k\sigma}^{\text{bf}}(\omega) \approx \frac{e^2 \Omega}{2\pi c m_e^2 \omega} \int d\mathbf{k}' \left\langle \left| p_{\mathbf{k}'k}^\sigma \right|^2 \right\rangle \delta\left(\frac{\hbar^2 k'^2}{2m_e} - \tilde{\epsilon}_{k\sigma}(t) - \hbar\omega\right)$$



Absorption coefficient

$$\kappa_{\text{abs}}(\omega) \equiv n_{\text{atom}} \frac{1}{N} \left\{ \sum_{kk'\sigma} \sigma_{kk'\sigma}^{\text{abs}}(\omega) [f_{k'\sigma}(t) - f_{k\sigma}(t)] + \sum_{k\sigma} \sigma_{k\sigma}^{\text{bf}}(\omega) f_{k\sigma}(t) \right\}$$

bulk atomic density

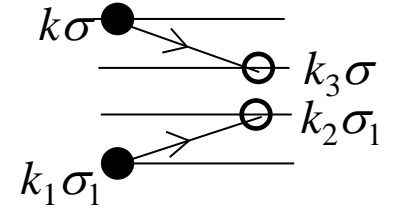
cluster size

Boltzmann collision term

$$\left. \frac{\partial f_{k\sigma}(t)}{\partial t} \right]_{\text{coll}} \approx -\frac{\pi}{\hbar} \sum_{k_1 k_2 k_3 \sigma_1} V_{kk_3 k_1 k_2}^{\sigma\sigma_1} \left(V_{k_3 k k_2 k_1}^{\sigma\sigma_1} - \delta_{\sigma\sigma_1} V_{k_2 k k_3 k_1}^{\sigma\sigma} \right)$$

$$\times \left[f_{k\sigma}(t) f_{k_1\sigma_1}(t) (1 - f_{k_2\sigma_1}(t)) (1 - f_{k_3\sigma}(t)) - (1 - f_{k\sigma}(t)) (1 - f_{k_1\sigma_1}(t)) f_{k_2\sigma_1}(t) f_{k_3\sigma}(t) \right]$$

$$\times \frac{1}{\pi} \frac{\Gamma'}{\left(\tilde{\varepsilon}_{k_3\sigma}(t) + \tilde{\varepsilon}_{k_2\sigma_1}(t) - \tilde{\varepsilon}_{k_1\sigma_1}(t) - \tilde{\varepsilon}_{k\sigma}(t) \right)^2 + \Gamma'^2} + cc$$



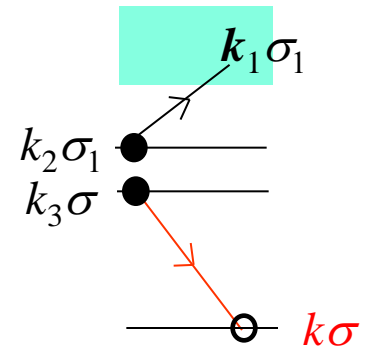
Γ' : free parameter

Auger decay

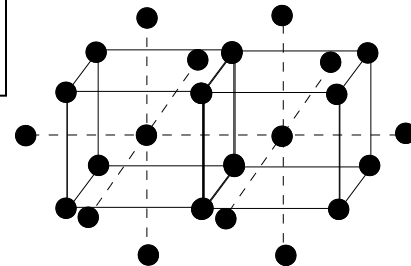
$$\left. \frac{\partial f_{k\sigma}}{\partial t} \right]_{\text{Auger}} = \frac{1}{\tau_{\text{Auger}}^{\text{in}}(k\sigma)} [1 - f_{k\sigma}(t)] - \left[\frac{1}{\tau_{\text{Auger}}^{\text{out}}(k\sigma)} + \frac{1}{\tau_{\text{Auger}}^{\text{out, cont}}(k\sigma)} \right] f_{k\sigma}(t)$$

$$\frac{1}{\tau_{\text{Auger}}^{\text{in}}(k\sigma)} \approx \frac{\pi}{\hbar} \frac{\Omega}{(2\pi)^3} \sum_{k_2 k_3 \sigma_1} \int d\mathbf{k}_1 V_{kk_3 \mathbf{k}_1 k_2}^{\sigma\sigma_1} \left(V_{k_3 k k_2 \mathbf{k}_1}^{\sigma\sigma_1} - \delta_{\sigma\sigma_1} V_{k_3 \mathbf{k}_1 k_2 k}^{\sigma\sigma} \right) f_{k_2\sigma_1}(t) f_{k_3\sigma}(t)$$

$$\times \delta \left(\tilde{\varepsilon}_{k_3\sigma}(t) + \tilde{\varepsilon}_{k_2\sigma_1}(t) - \frac{\hbar^2 k_1^2}{2m_e} - \tilde{\varepsilon}_{k\sigma}(t) \right) + cc$$

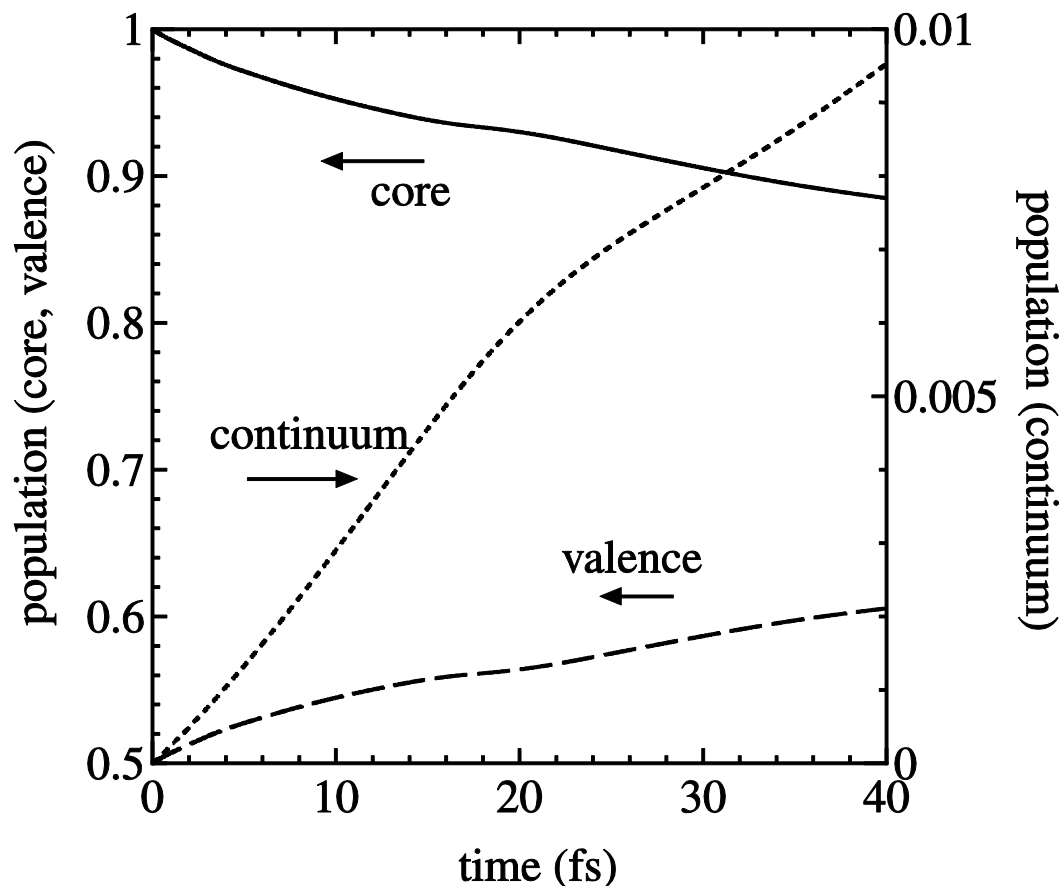


NUMERICAL RESULTS FOR LITHIUM



Population kinetics

$$E_v = 60 \text{ eV}, I_v = 10^{14} \text{ W/cm}^2$$



$$\phi_i(\mathbf{r}) : i = 1s, 2s, 2p$$

$$\hbar\omega_v = 60 \text{ eV}$$

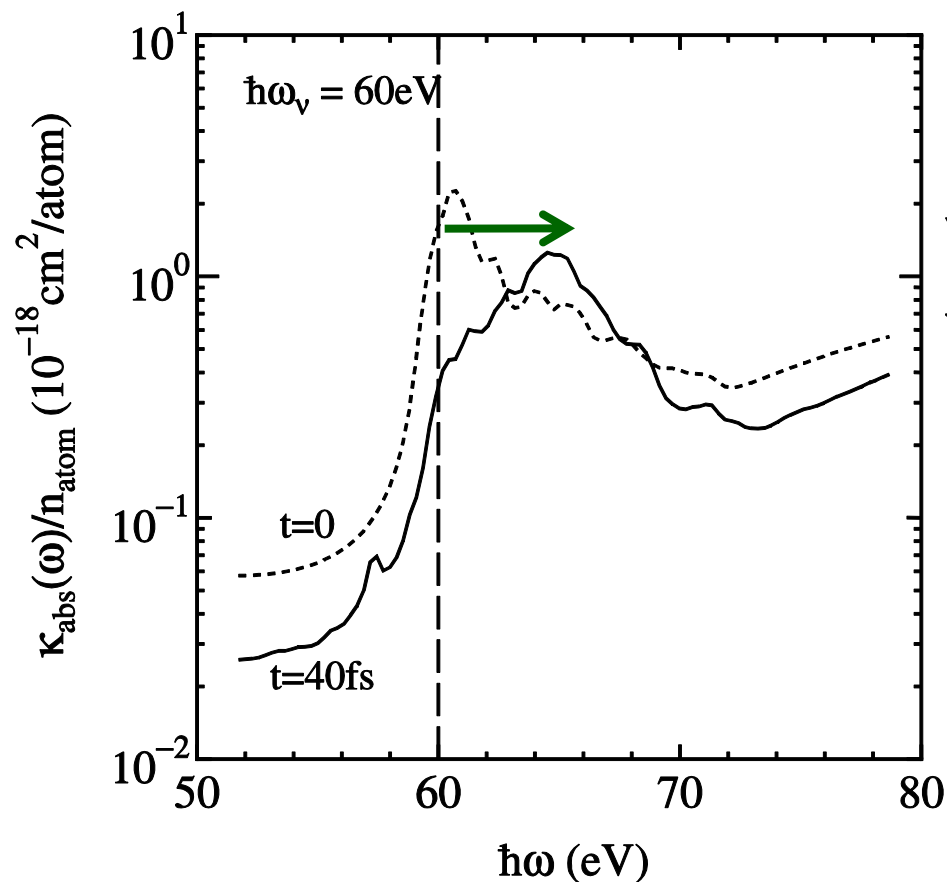
$$I_v = 10^{14} \text{ W/cm}^2$$

$$\Gamma = \Gamma' = 0.3 \text{ eV}$$

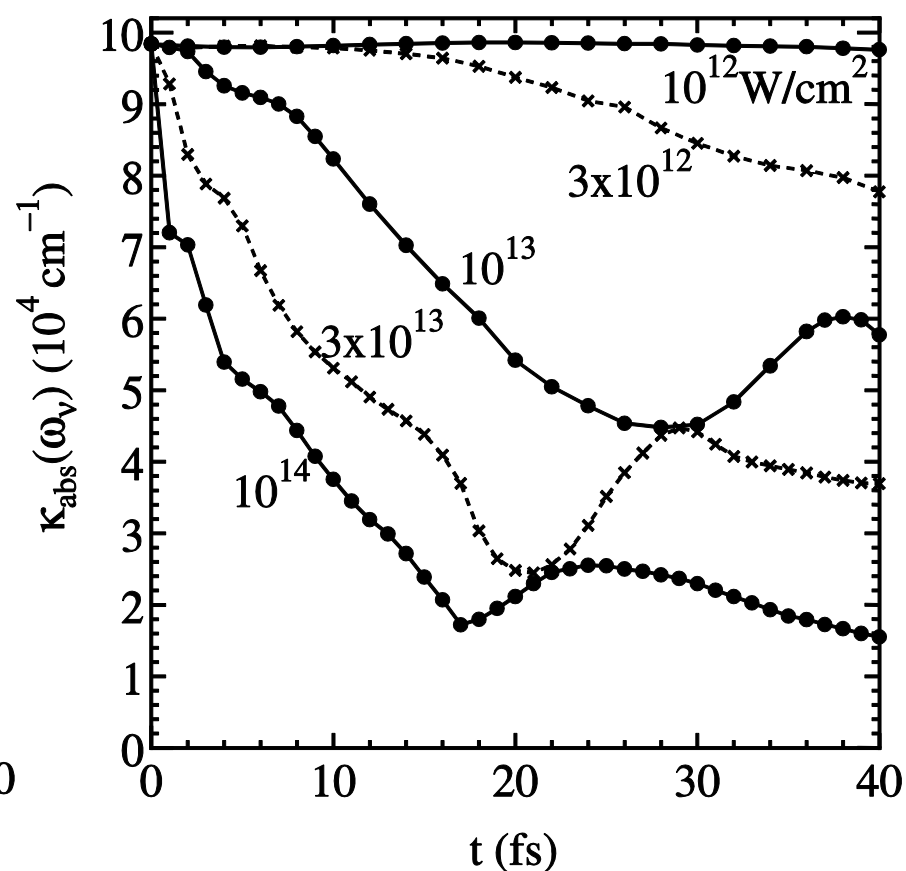
$$n = 4.75 \times 10^{22} \text{ cm}^{-3}$$

**11% of core electrons
excited within 40 fs**

Photoabsorption spectra



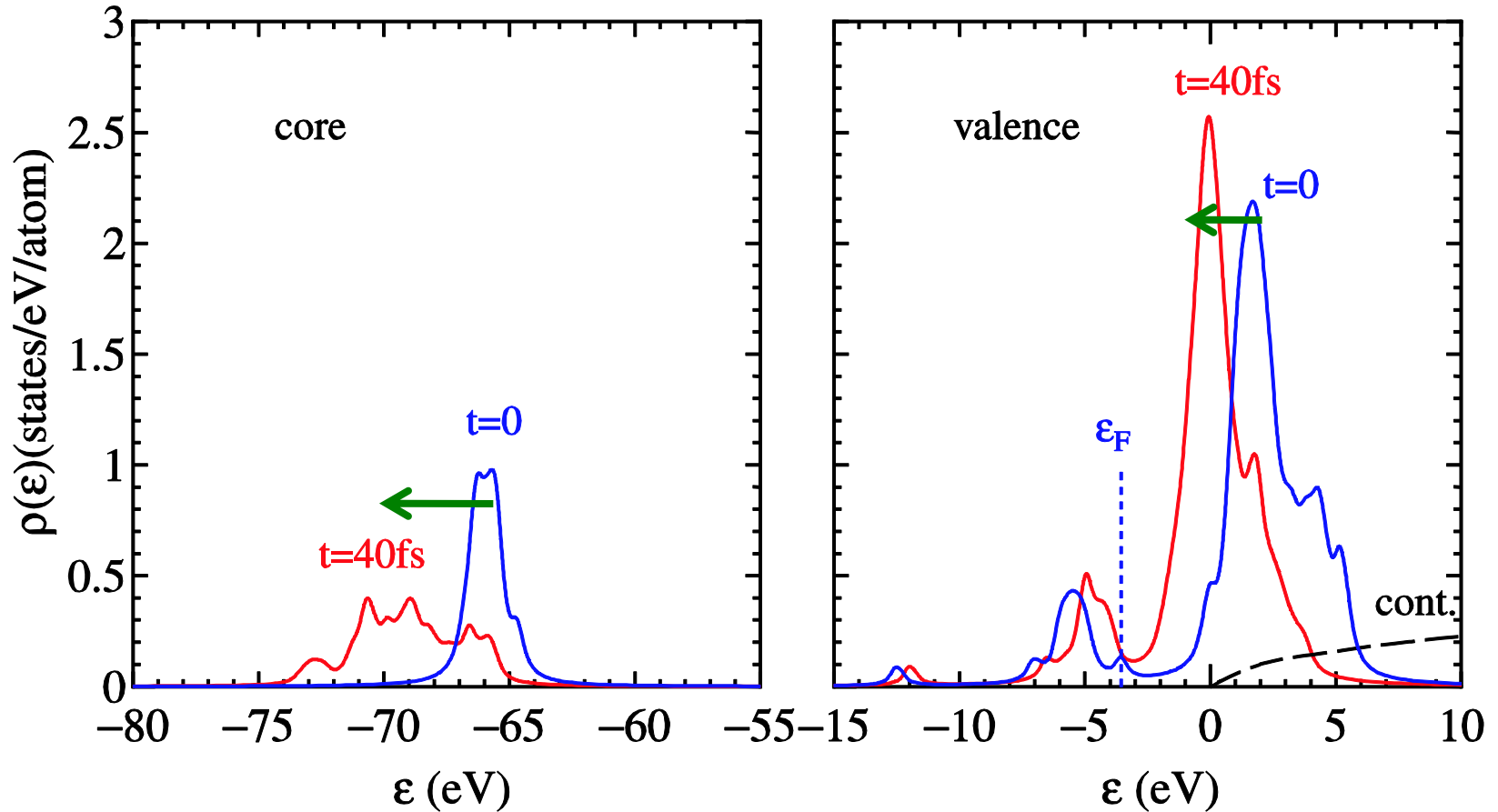
Absorption coefficient at $\omega = \omega_v$



Absorption edge shift \rightarrow Decrease of absorption within 10 fs

Density of states

$$\rho(\varepsilon) = \frac{1}{N\pi} \sum_{k=1}^{N_{MO}} \sum_{\sigma=\alpha,\beta} \frac{\Gamma}{[\varepsilon - \tilde{\varepsilon}_{k\sigma}(t)]^2 + \Gamma^2}$$



**Lowering of core levels relative to the valence levels
→ red shift of the absorption edge**

Nonlinear transmission due to K-edge shift

$$\frac{\partial I(z,t)}{\partial z} = -\kappa_{\text{abs}}(I(z;t))I(z,t)$$

local absorption coefficient

