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Density-matrix approach to core-level photoexcitation of metals

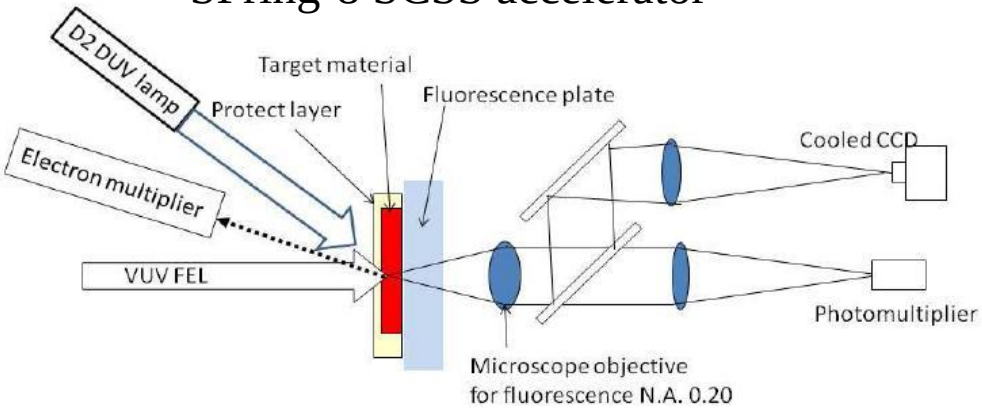
Hikaru Kitamura

Department of Physics, Kyoto University, Japan

Nonlinear transmission of VUV FEL pulse through Sn

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

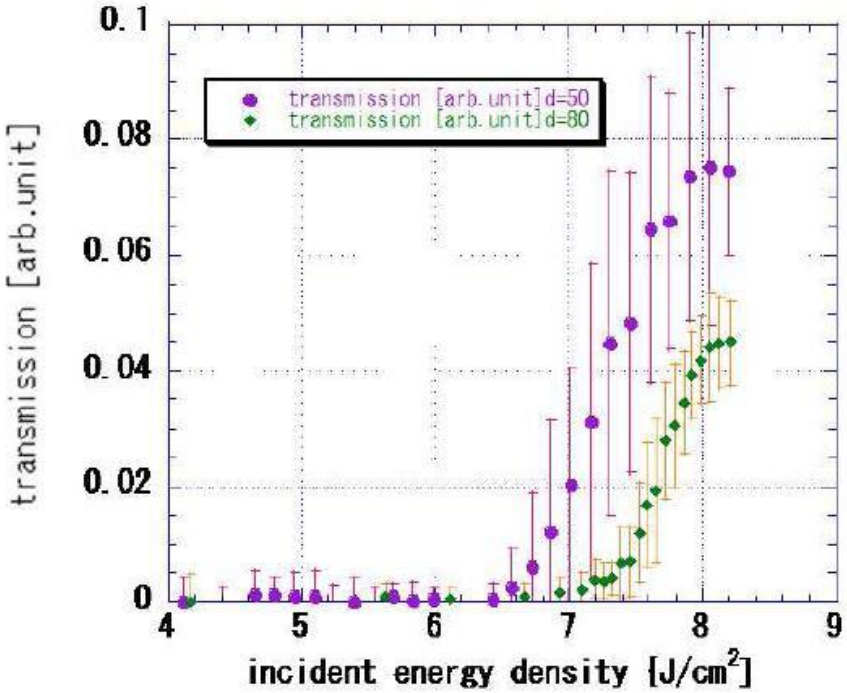
SPring-8 SCSS accelerator

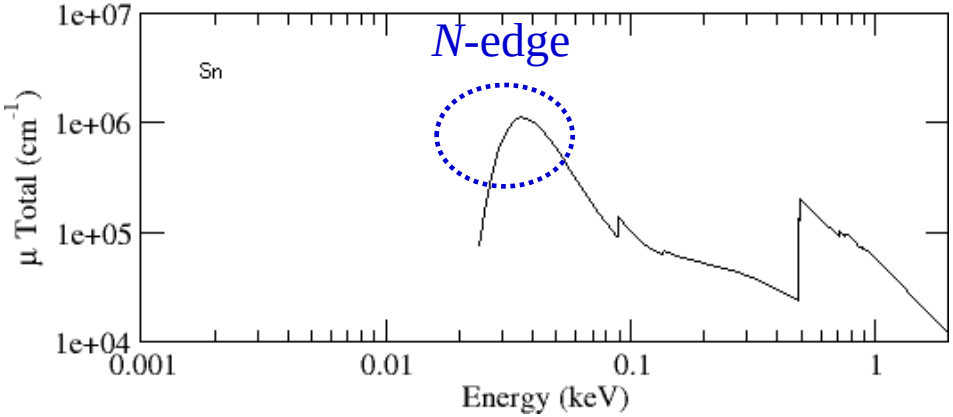


Sn target (50-80 nm thickness)

$\hbar\omega_v$ = 20-25 eV

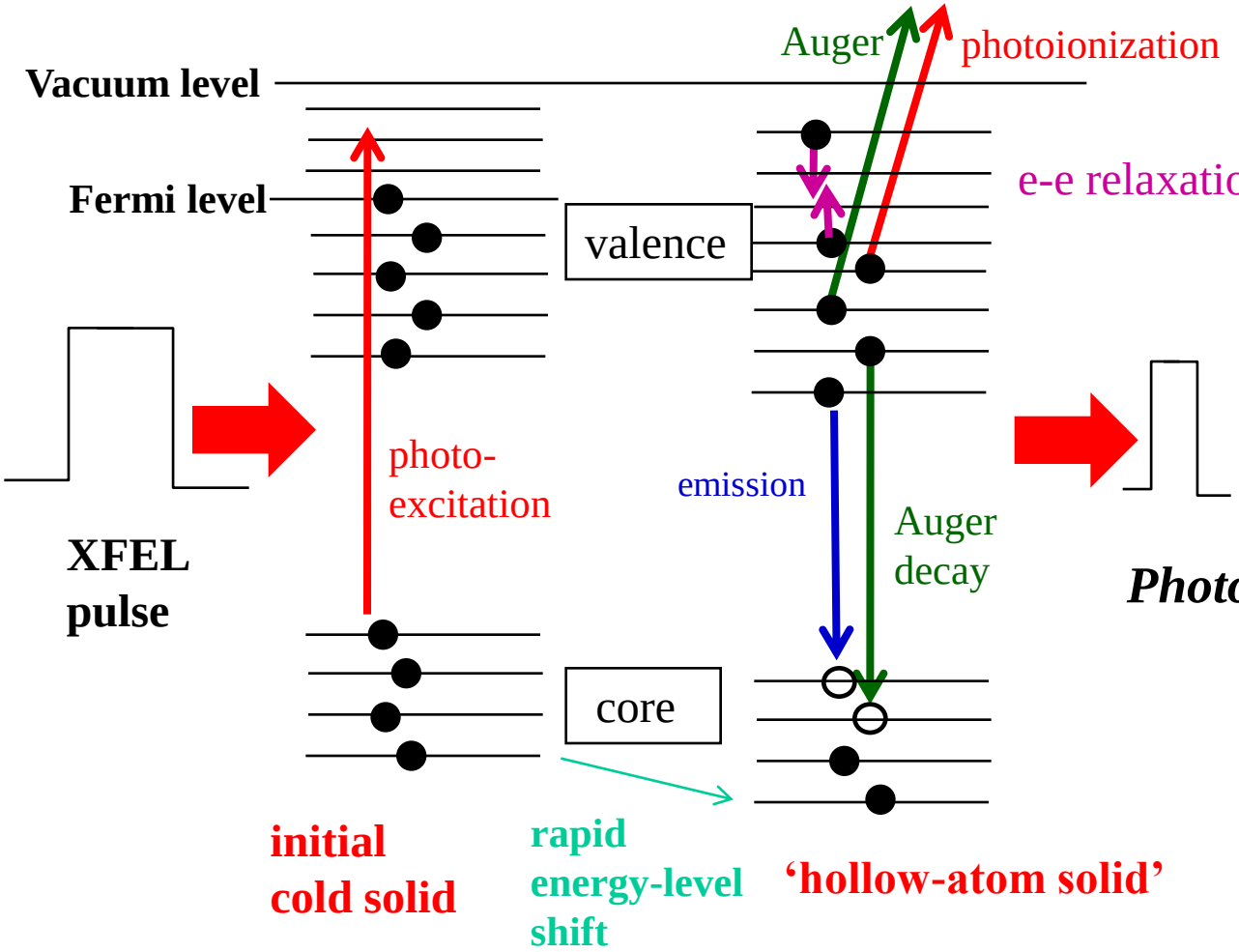
Δt = 100 fs





Saturable absorption in VUV range

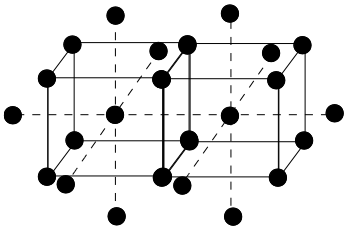
Simulation of elementary processes in highly core-excited metals



transmitted pulse shape ?

Photonic device for X-rays

cluster model



molecular orbitals (MOs)

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

Slater-type atomic orbital

$\sigma =$ α (up spin)
β (down spin)

Total Hamiltonian

MO energy levels (unrestricted Hartree-Fock calculation)

$$H = \sum_{k\sigma} \varepsilon_k^{\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} - \sum_{k_1 k_2 \sigma} \sum_{k_3 \sigma'}^{\text{occ}} \left(V_{k_1 k_2 k_3 k_3}^{\sigma\sigma'} - \delta_{\sigma\sigma'} V_{k_1 k_2 k_3 k_3}^{\sigma\sigma'} \right) c_{k_1\sigma}^{\dagger} c_{k_2\sigma}$$

$$+ \frac{1}{2} \sum_{\substack{k_1 k_2 k_3 k_4 \\ \sigma\sigma'}} V_{k_1 k_2 k_3 k_4}^{\sigma\sigma'} c_{k_1\sigma}^{\dagger} c_{k_3\sigma'}^{\dagger} c_{k_4\sigma'} c_{k_2\sigma} + \frac{e}{m_e c} \mathbf{A}(t) \bullet \sum_{k_1 k_2 \sigma} \mathbf{p}_{k_1 k_2}^{\sigma} c_{k_1\sigma}^{\dagger} c_{k_2\sigma}$$

electron-electron interaction

electron-photon interaction

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

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

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

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

Density matrix equation for electron dynamics

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

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

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

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

$$K^{\sigma\sigma_1}_{kk_3k_1k_2} \equiv \left\langle c^{\dagger}_{k\sigma} c^{\dagger}_{k_1\sigma_1} c_{k_2\sigma_1} c_{k_3\sigma} \right\rangle \quad \text{two-particle density matrix}$$

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

correlation

Born approximation + exchange

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

Effects of electron-hole interaction

$$\tilde{\varepsilon}_{kk'\sigma}(t) \equiv \sum_{k_1 k_2 \sigma_1} \left(V^{\sigma\sigma_1}_{kk'k_1k_2} - \delta_{\sigma\sigma_1} V^{\sigma\sigma}_{kk_2k_1k'} \right) \left[\left\langle \rho_{k_1k_2\sigma}(t) \right\rangle - \delta_{k_1k_2} \delta^{\mathrm{occ}}_{k_1\sigma_1} \right]$$

self-energy matrix

$$V^{\sigma\sigma_1}_{kk_3k_1k_2} \approx \begin{cases} \sum_{ij\mu} \sum_{i'j'\mu'} c^{\sigma *}_{k,i\mu} c^{\sigma}_{k_3,j\mu} c^{\sigma_1 *}_{k_1,i'\mu'} c^{\sigma_1}_{k_2,j'\mu'} \left(i\mu, j\mu \,|\, i'\mu', j'\mu' \right), & \text{for } \left| \mathbf{R}_\mu - \mathbf{R}_\mu{}' \right| \le R_{\mathrm{nn}} \\ 0, \text{ otherwise} \end{cases}$$

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 $k' \to k$

$$\hbar \tilde{\omega}^{\mathrm{IVO}}_{kk'\sigma}(t) \equiv \tilde{\varepsilon}_{k\sigma}(t) - \tilde{\varepsilon}_{k'\sigma}(t) - \underline{\left(V^{\sigma\sigma}_{k'k'kk} - V^{\sigma\sigma}_{k'kkk'} \right) \left[f_{k'\sigma}(t) - f_{k\sigma}(t) \right]}$$

(*e-h* attraction: *improved virtual orbital*)

(3) renormalized transition matrix in 'RPA+exchange'

$$\tilde{\mathbf{p}}^{\sigma}_{kk'}(\omega) = \mathbf{p}^{\sigma}_{kk'} + \sum_{\substack{k_1k_2\sigma_1 \\ (\neq kk'\sigma)}} \left(V^{\sigma\sigma_1}_{kk'k_2k_1} - \delta_{\sigma\sigma_1} V^{\sigma\sigma_1}_{kk_1k_2k'} \right) \frac{\omega - \tilde{\omega}^{\mathrm{IVO}}_{k_1k_2\sigma_1} - i\Gamma}{(\omega - \tilde{\omega}^{\mathrm{IVO}}_{k_1k_2\sigma_1})^2 + \Gamma^2} \left[f_{k_2\sigma_1}(t) - f_{k_1\sigma_1}(t) \right] \frac{\tilde{\mathbf{p}}^{\sigma_1}_{k_1k_2}(\omega)}{\hbar}$$

Markov approximation

↓

Generalized rate equation

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

$$\frac{\partial f_{k\sigma}(t)}{\partial t} = \frac{I_\nu}{\hbar\omega_\nu}\left[\sum_{k'(\neq k)} \sigma_{kk'\sigma}(\omega_\nu)\left[f_{k'\sigma}(t) - f_{k\sigma}(t)\right] - \sigma^{\mathrm{bf}}_{k\sigma}(\omega_\nu) f_{k\sigma}(t)\right]$$

radiative (bound-bound, bound-free)

$$+\left.\frac{\partial f_{k\sigma}(t)}{\partial t}\right]_{\mathrm{coll}} + \left.\frac{\partial f_{k\sigma}(t)}{\partial t}\right]_{\mathrm{Auger}}$$

e-e collision (intravalence, Auger)

$$I_\nu = \frac{\omega_\nu^2 \left|\mathbf{A}_0\right|^2}{8\pi c}$$

laser intensity

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

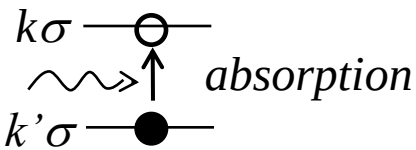
Radiative cross-sections

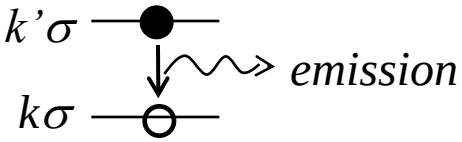
Bound-bound

averaged over polarization

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

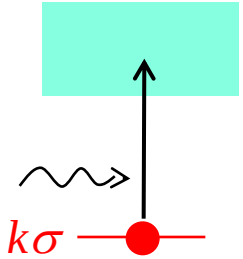
$$= \sigma^{\mathrm{abs}}_{kk'\sigma}(\omega) + \sigma^{\mathrm{emi}}_{kk'\sigma}(\omega)$$





Bound-free

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

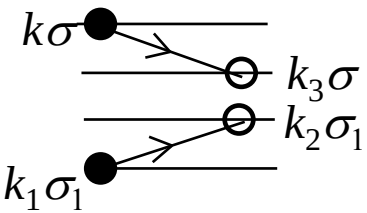


Absorption coefficient

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

bulk atomic density cluster size

Boltzmann collision term



$$\left.\frac{\partial f_{k\sigma}(t)}{\partial t}\right]_{\text{coll}} \approx -\frac{\pi}{\hbar}\sum_{k_1k_2k_3\sigma_1} V^{\sigma\sigma_1}_{kk_3k_1k_2}\left(V^{\sigma\sigma_1}_{k_3kk_2k_1} - \delta_{\sigma\sigma_1}V^{\sigma\sigma}_{k_2kk_3k_1}\right)$$

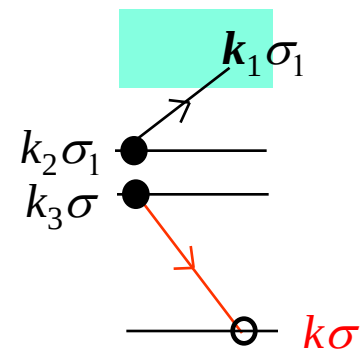
$$\times\left[f_{k\sigma}(t)\,f_{k_1\sigma_1}(t)\left(1-f_{k_2\sigma_1}(t)\right)\left(1-f_{k_3\sigma}(t)\right)-\left(1-f_{k\sigma}(t)\right)\left(1-f_{k_1\sigma_1}(t)\right)f_{k_2\sigma_1}(t)\,f_{k_3\sigma}(t)\right]$$

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

Γ': free parameter

Auger decay

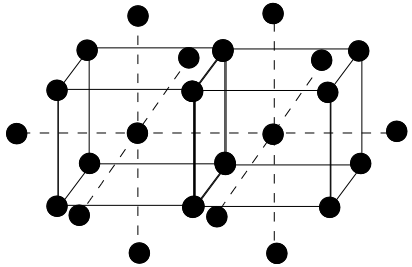
$$\left.\frac{\partial f_{k\sigma}}{\partial t}\right]_{\text{Auger}} = \underbrace{\frac{1}{\tau^{\text{in}}_{\text{Auger}}(k\sigma)}\left[1-f_{k\sigma}(t)\right]}_{\text{incoming}} - \underbrace{\left[\frac{1}{\tau^{\text{out}}_{\text{Auger}}(k\sigma)}+\frac{1}{\tau^{\text{out, cont}}_{\text{Auger}}(k\sigma)}\right]f_{k\sigma}(t)}_{\text{outgoing}}$$



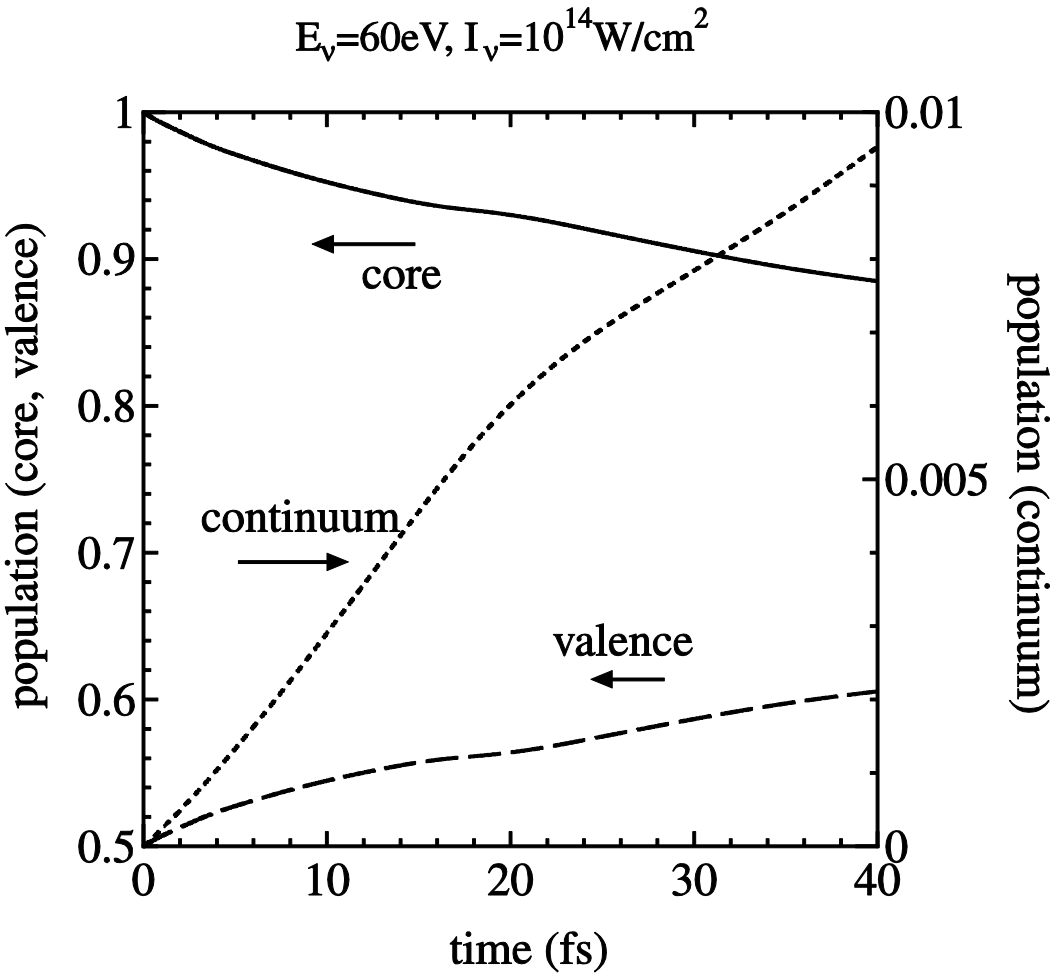
$$\frac{1}{\tau^{\text{in}}_{\text{Auger}}(k\sigma)} \simeq \frac{\pi}{\hbar}\frac{\Omega}{(2\pi)^3}\sum_{k_2k_3\sigma_1}\int d\mathbf{k}_1 V^{\sigma\sigma_1}_{kk_3\mathbf{k_1}k_2}\left(V^{\sigma\sigma_1}_{k_3kk_2\mathbf{k_1}} - \delta_{\sigma\sigma_1}V^{\sigma\sigma}_{k_3\mathbf{k_1}k_2k}\right)f_{k_2\sigma_1}(t)\,f_{k_3\sigma}(t)$$

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

NUMERICAL RESULTS FOR LITHIUM



Population kinetics



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

$\hbar\omega_\nu$ = 60 eV

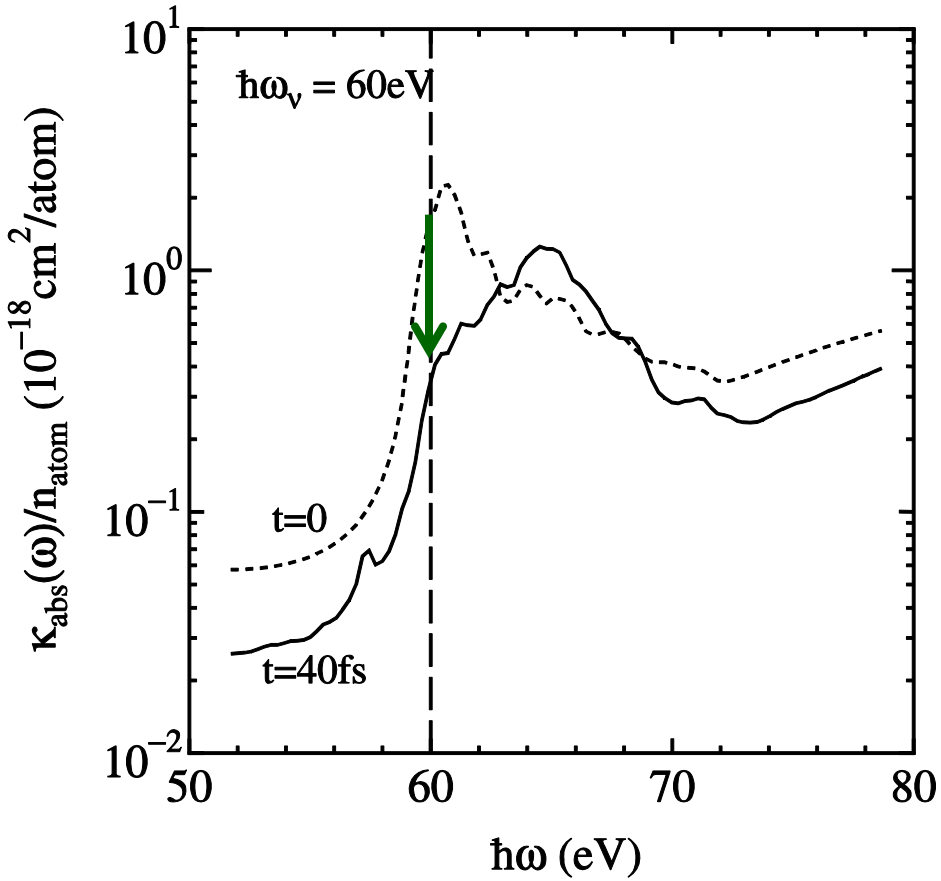
I_ν = 10^{14} W/cm^2

$\Gamma = \Gamma' = 0.3$ eV

$n = 4.75\times10^{22}$ cm^{-3}

11% of core electrons excited within 40 fs

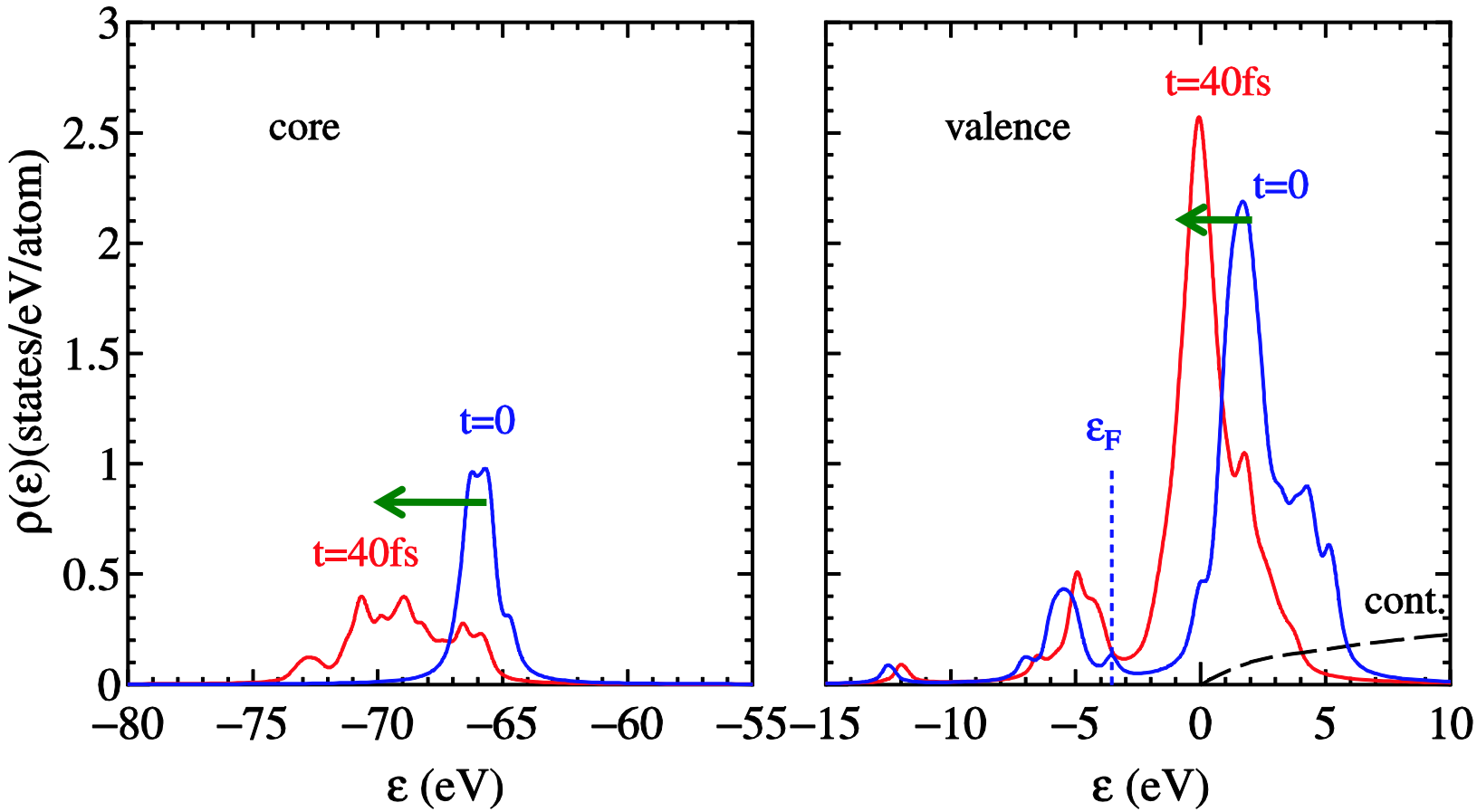
Time-resolved photoabsorption spectra



Blue shift of the edge → decrease of absorption

Density of states

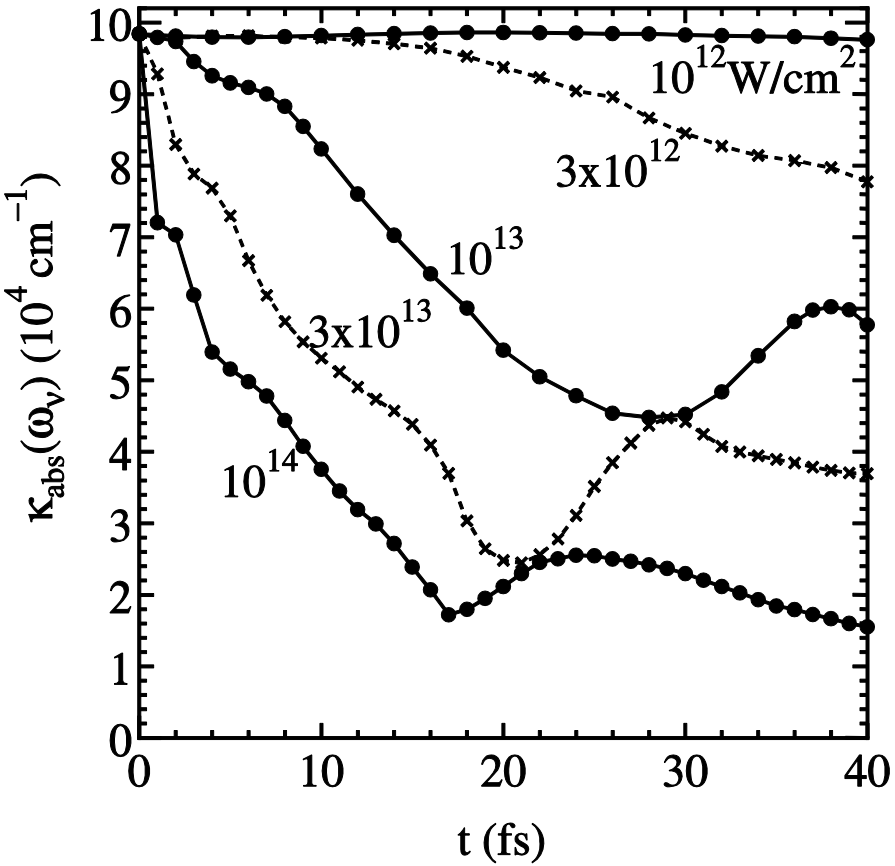
$$\rho(\varepsilon) = \frac{1}{N\pi} \sum_{k=1}^{N_{\mathrm{MO}}} \sum_{\sigma=\alpha,\beta} \frac{\Gamma}{\left[\varepsilon - \tilde{\varepsilon}_{k\sigma}(t)\right]^2 + \Gamma^2}$$



<u>Lowering</u> of core levels relative to the valence levels

→ <u>red shift</u> of the absorption edge

Absorption coefficient vs time

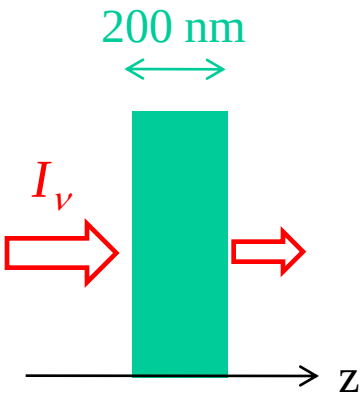


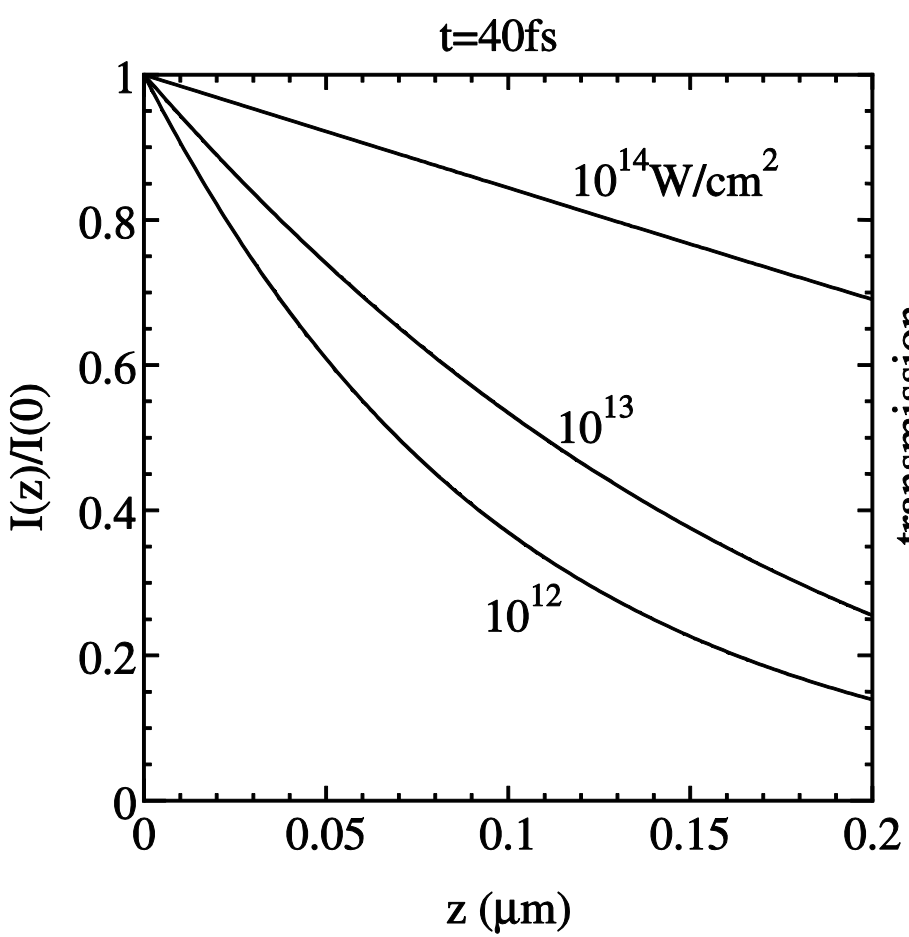
Nonlinear transmission

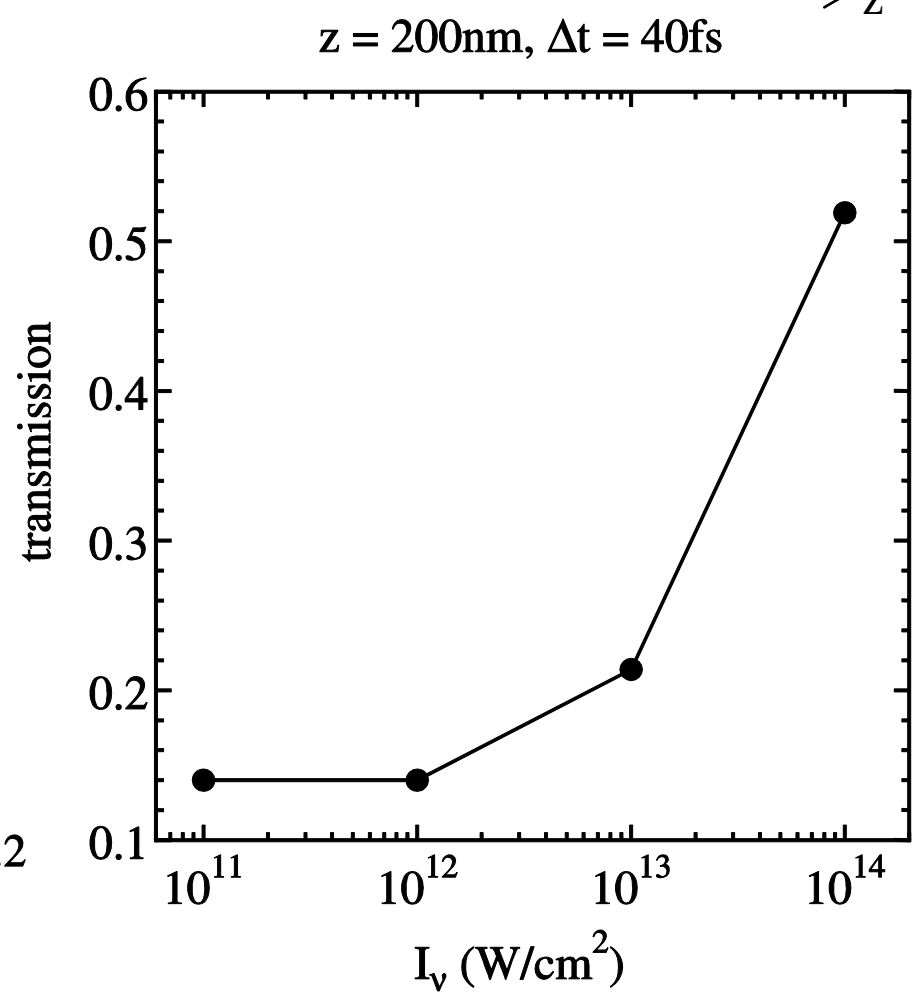
$$\frac{\partial I(z,t)}{\partial z} = -\kappa_{\text{abs}}\big(I(z;t)\big)\,I(z,t)$$

local absorption coefficient

Li sample







OUTSTANDING ISSUES

(1) Absorption edge shift --- blue shift or red shift ?

- Optical excitation of semiconductors

  → band gap narrowing (red shift)

- Metallic lithium K-edge excitation

  → blue shift

<u>screening effect</u>

(2) Shake-up effect

(3) Pulse propagation (Maxwell eq.)