Anomalous transient blueshift in the internal stretch mode of CO/Pd(111))

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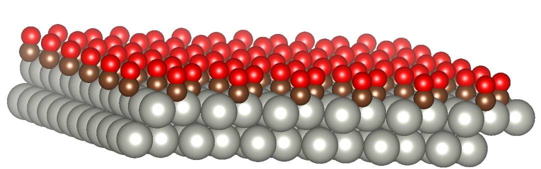
Université de Bordeaux (UBx)

September 25, 2024

Motivation



R. Bombín, A. S. Muzas, D. Novko, J. I. Juaristi, and M. Alducin

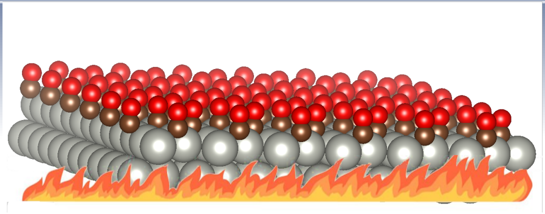
Phys. Rev. B 107, L121404 (2023)

Phys. Rev. B 108, 045409 (2023)

Metallic surfaces covered with polar molecules

- The internal stretch mode is measured with pump-probe infrared spectroscopy with a resolution of femtoseconds.
- In our case we study the Pd(111) surface with 0.5 ML of CO

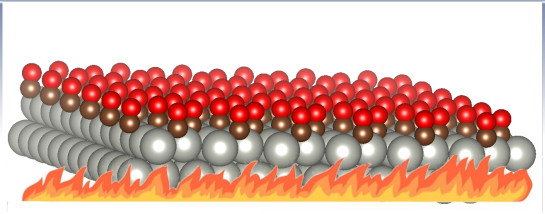
Motivation



Thermal heating

- **Thermal equilibrium**
- Changes in the internal stretch mode

Motivation



Thermal heating

- **Thermal equilibrium**
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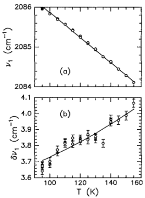
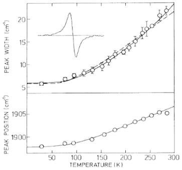
CO/Cu(100)



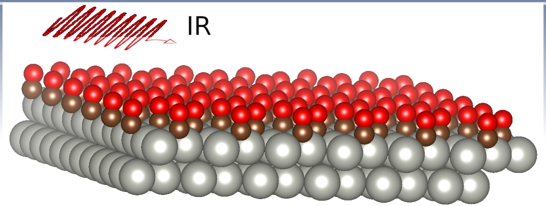
Gremer et al. J. Chem. Phys 101 1704 (1994)

CO/Ni(111)



Person *et al*. PRL **54**, 2119-2122 (1985)

Motivation



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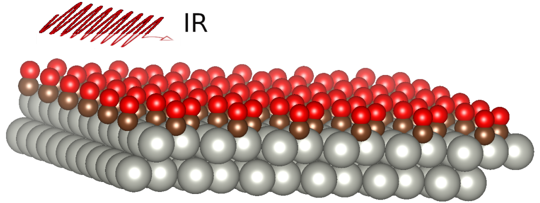
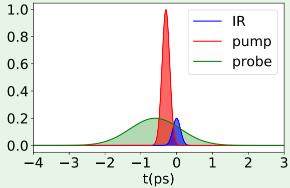


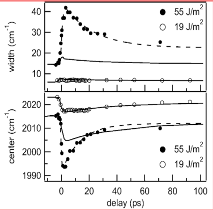
Pump-probe femtosecond spectroscopy

1. Low intensity IR pulse –> phase coherence $F \sim 15\mu\text{J/m}^2$, $\Delta\tau \sim 150$ fs, $\lambda = 800nm$
2. Pump UV pulse $F \in [10 - 200]\text{J/m}^2$, $\Delta\tau \sim 150$ fs, $\lambda = 400nm$
3. Probe pulse The internal stretch mode is tracked



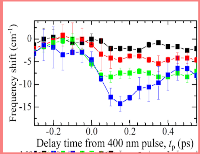
Pump-probe experimental results

CO/Ru(0001)



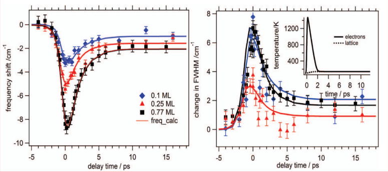
Bonn *et al.* PRL **84** 4653 (2000)

CO/Cu(100)



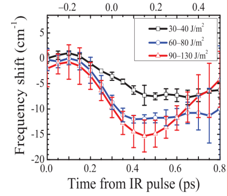
Innoue *et al.* PRL **117**, 186101 (2016)

CO/Cu(110)



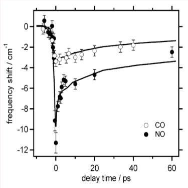
Omiya *et al.* JCP **141**, 214705 (2014)

CO/Pt(111)



Inoue *et al.* JCP 137, 024704 (2012)

CO and NO on Ir(111)



Lane *et al.* JCPC 111, 14198 (2007)

Pump-probe experimental results

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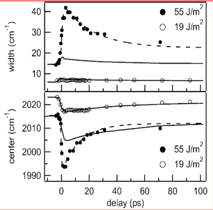
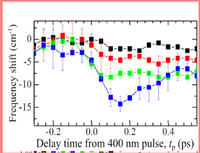
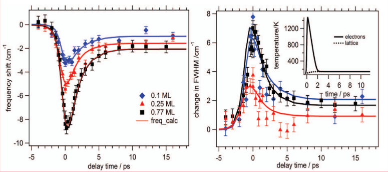


CO/Cu(100)



Innoue *et al.* PRL **117**, 186101 (2016)

CO/Cu(110)

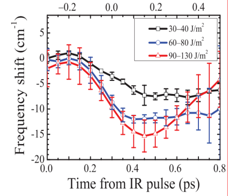


Omiya *et al.* JCP **141**, 214705 (2014)

Always redshift??

- FCC and HCP Transition metals
- Different surfaces: (111), (100)...
- Different coverages
- Different adsorbates: CO and NO
- Different lasers

CO/Pt(111)



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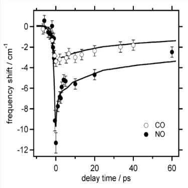

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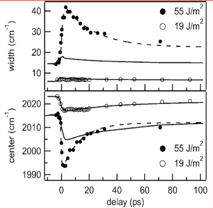

Bonn *et al*. PRL **84** 4653 (2000)

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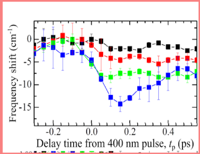
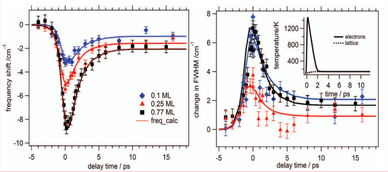


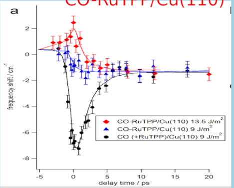
Innoue *et al*. PRL **117**, 186101 (2016)

CO/Cu(110)



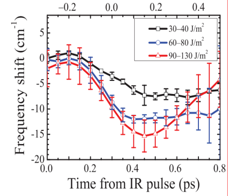
Omiya *et al*. JCP **141**, 214705 (2014)

CO-RuTPP/Cu(110)



Lane *et al* Surfaces **2**,117130 (2019)

CO/Pt(111)



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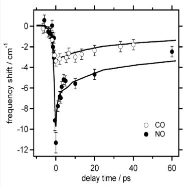

Lane *et al*. JCPC 111, 14198 (2007)

Method

Phonon self-energy $\pi(\omega) = \pi^{[1]}(\omega) + \pi^{[2]}(\omega)$

Novko *et al.* PRL **122** 016806 (2019)

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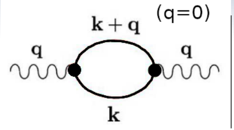
- interband $\propto g^2$



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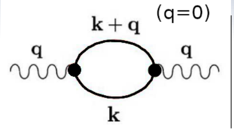

$$\pi_\lambda^{[1]} = \sum_{\mu,\mu',\mathbf{k}} \left| g_\lambda^{\mu,\mu'}(\mathbf{k}, 0) \right|^2 \frac{f(\epsilon_{\mu,\mathbf{k}}) - f(\epsilon_{\mu',\mathbf{k}})}{\omega_\lambda - \epsilon_{\mu,\mathbf{k}} - \epsilon_{\mu',\mathbf{k}} + i\eta}$$

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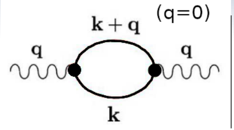

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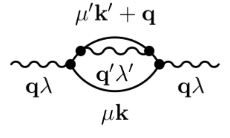

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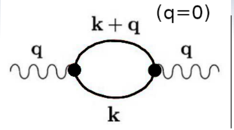

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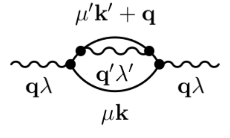
$$\pi_\lambda^{[2]}(\omega_\lambda) = -\sum_{\substack{\mu\mu'\mathbf{k}\sigma,\lambda'\mathbf{k}' \\ s,s'=\pm 1}} |g_\lambda^{\mu\mu}(\mathbf{k},0)|^2 \left| g_{\lambda'}^{\mu\mu'}(\mathbf{k},\mathbf{q}') \right|^2$$

$$\times \frac{f(\epsilon_{\mu,\mathbf{k}}) - f(\epsilon_{\mu',\mathbf{k}'} - s's\omega_{\mathbf{q}',\lambda'})}{\epsilon_{\mu,\mathbf{k}} - (\epsilon_{\mu',\mathbf{k}'} - s's\omega_{\mathbf{q}'\lambda'})} \frac{s\left[n_b(s\omega_{\mathbf{q}'\lambda'}) + f(s'\epsilon_{\mu',\mathbf{k}'})\right]}{\omega_\lambda\left[\omega_\lambda + i\eta + s'(\epsilon_{\mu,\mathbf{k}} - \epsilon_{\mu',\mathbf{k}'}) + s\omega_{\mathbf{q}'\lambda'}\right]},$$



- intraband $\propto g^4$

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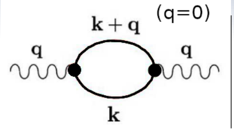

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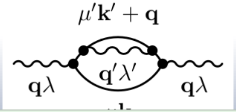

- intraband $\propto g^4$

Frequency shift $\Delta\omega$ and linewidth γ

$$\Delta\omega = \mathrm{Re}\pi_\lambda(\omega_\lambda) \qquad \gamma = -2\mathrm{Im}\pi_\lambda(\omega_\lambda)$$

Method

- electronic states at DFT level
- phonons from DFT perturbation theory
- electron-phonon coupling using many-bodymany-body perturbation theory

In second quantization

$$\hat{H} = \hat{H}_e + \hat{H}_{ph} + \hat{H}_{e-ph}$$

$$\hat{H} = \sum_{n,\mathbf{k}} \epsilon_{n,\mathbf{k}} \hat{c}^{\dagger}_{n,\mathbf{k}} \hat{c}_{n,\mathbf{k}} + \sum_{\nu,\mathbf{q}} \hbar\omega_{\nu,\mathbf{q}} (\hat{a}^{\dagger}_{\nu,\mathbf{q}} \hat{a}_{\nu,\mathbf{q}} + 1/2)$$

$$+ N^{-1} \sum_{\mathbf{k},\mathbf{q},m,n,\nu} g^{m,n}_{\nu}(\mathbf{k},\mathbf{q}) \hat{c}^{\dagger}_{m,\mathbf{k}+\mathbf{q}} \hat{c}_{n,\mathbf{k}} (\hat{a}_{\nu,\mathbf{q}} + \hat{a}^{\dagger}_{\nu,\text{-}\mathbf{q}})$$

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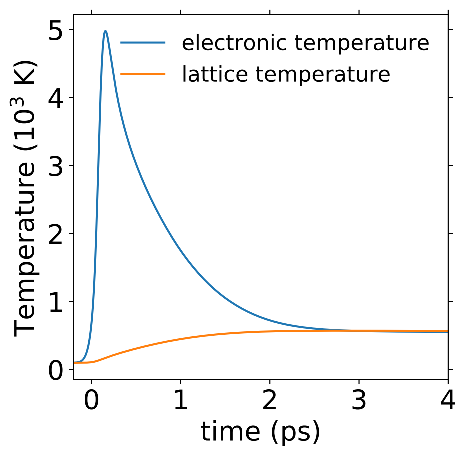
Method - time dependence



$$C_e \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z}\left(\kappa_e \frac{\partial T_e}{\partial z}\right) - G(T_e - T_l) + S$$

$$C_l \frac{\partial T_l}{\partial t} = G(T_e - T_l),$$

Input parameters

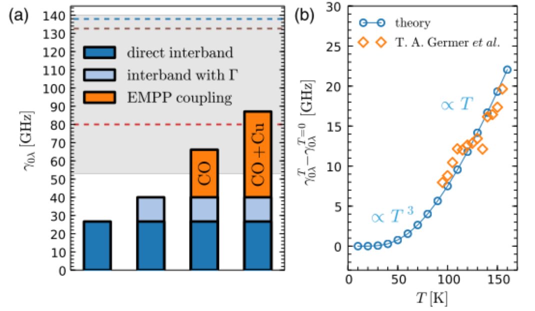
- Heat capacities C_e and C_l.
- thermal conductivity κ_e
- electron-phonon energy exchange coupling constant G

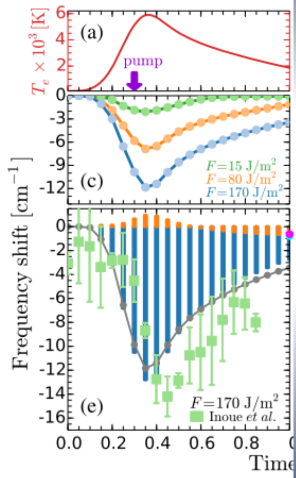
We use the values obtained by ab-initio by Li and Ji Comp. Mater. Sci. 202 110959 (2022)

Previos results for CO/Cu(100)

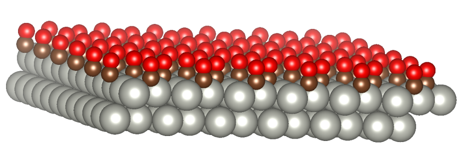
References:

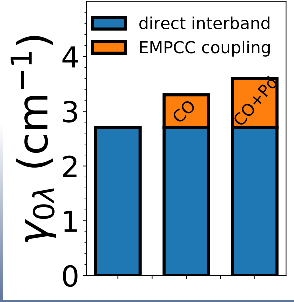
D. Novko *et al* Phys. Rev. Lett. **120** 156804 (2018)
D. Novko *et al* Phys. Rev. Lett. **122** 016806 (2019)

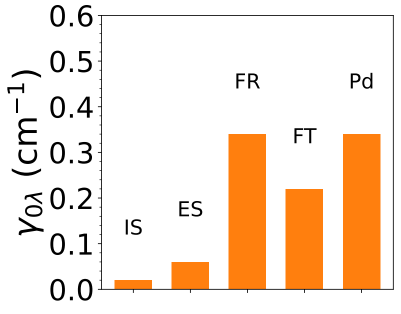




CO/Pd(111) - Low temperature linewidth







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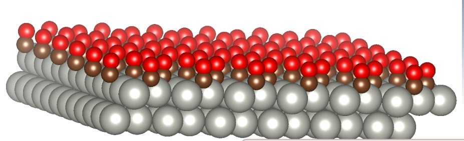
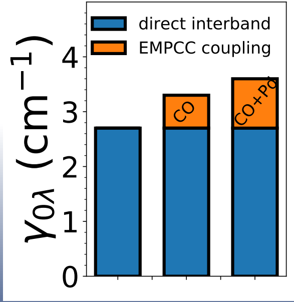
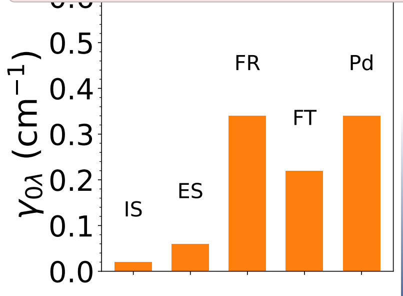
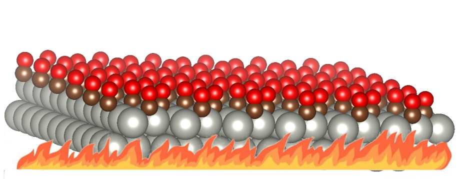




Quite similar to CO/Cu(100) results



CO/Pd(111) - heat



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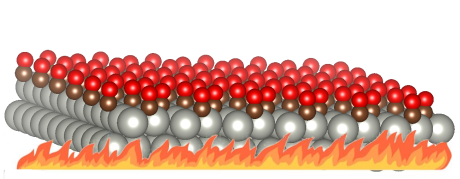
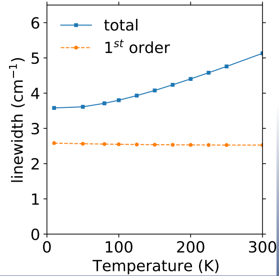
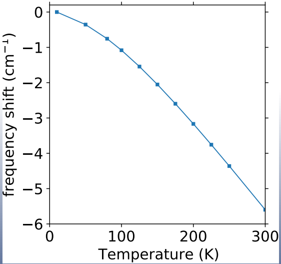
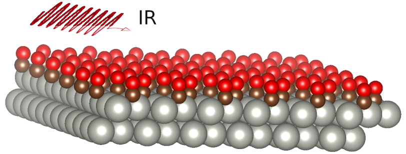






CO/Pd(111) pump-probe experimental conditions



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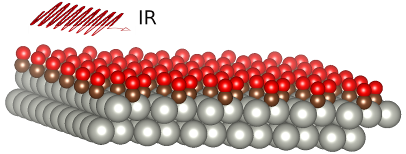

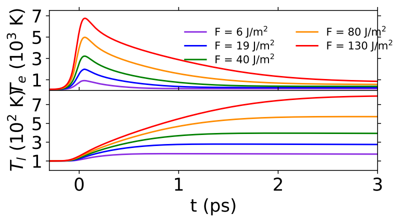

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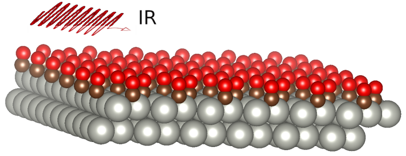
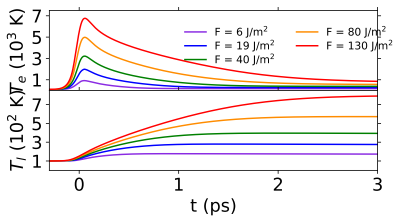
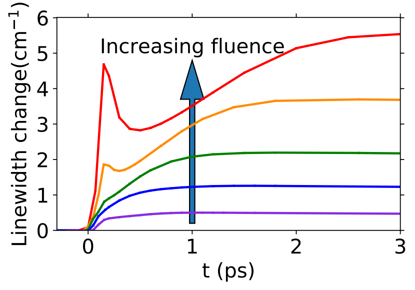
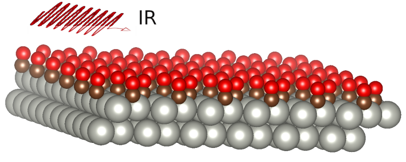
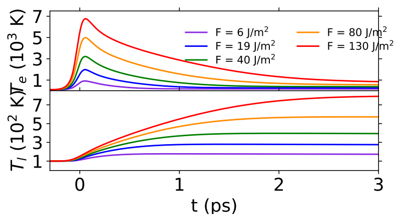


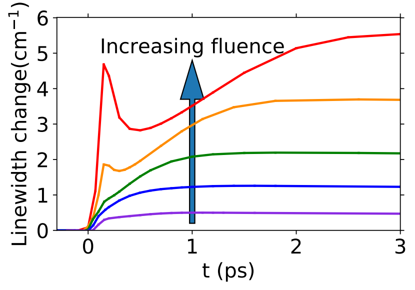


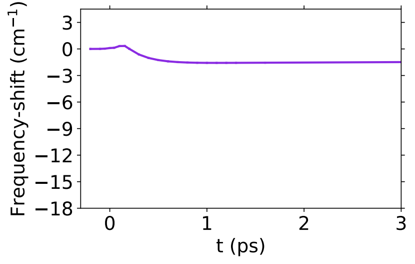


CO/Pd(111) pump-probe experimental conditions









CO/Pd(111)
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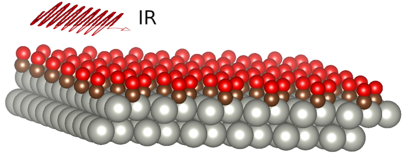

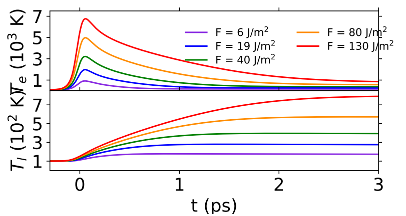

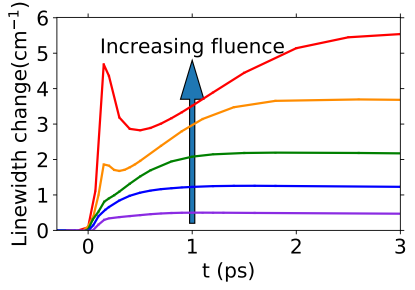

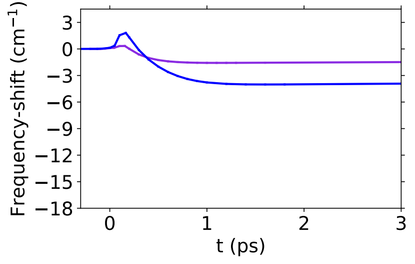

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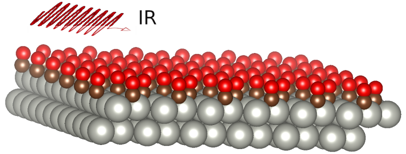

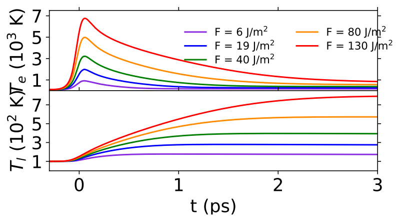

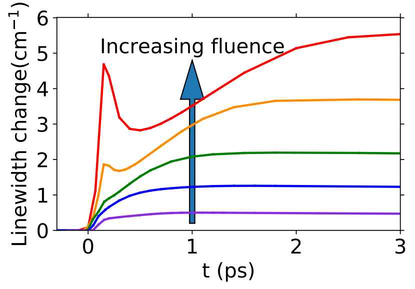

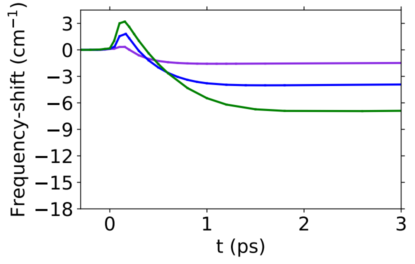

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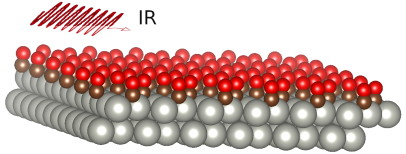

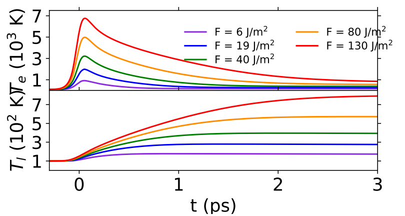

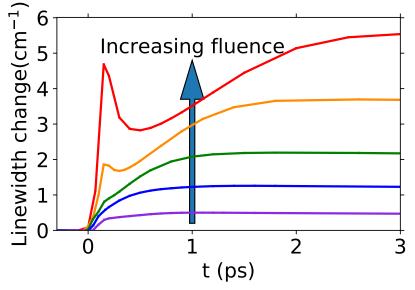

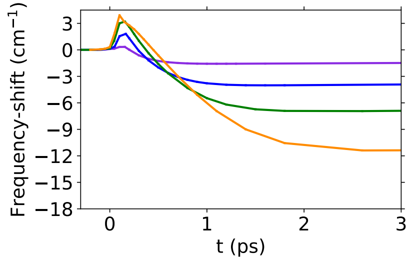

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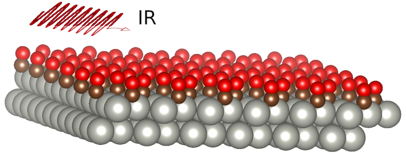

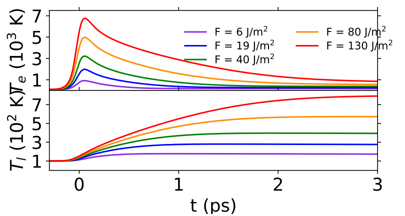

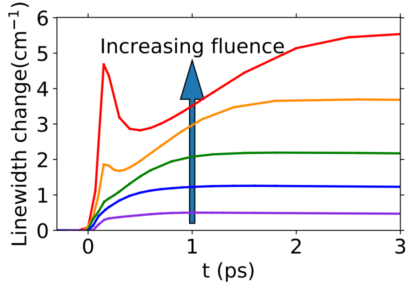

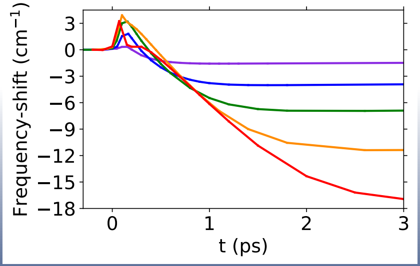

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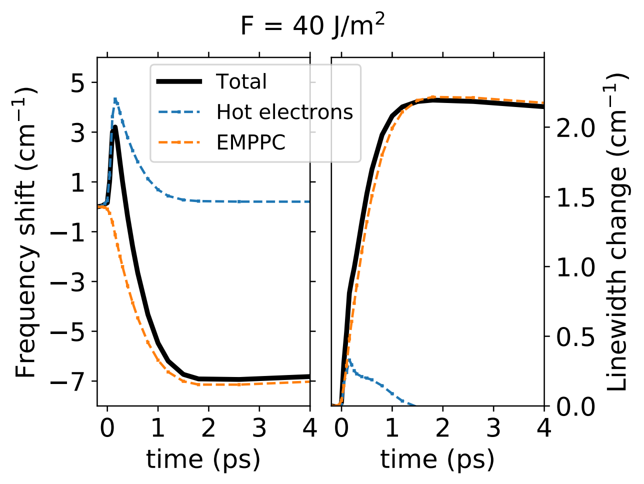
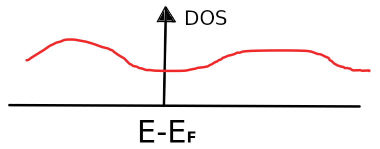


Where does the blue-shift comes from?



Usually, $\mathrm{Re}[\pi^{[1]}]$ is increased as T_e does

$$\pi_\lambda^{[1]} = \sum_{\mu,\mu',\mathbf{k}} \left|g_\lambda^{\mu,\mu'}(\mathbf{k},0)\right|^2 \frac{f(\epsilon_{\mu,\mathbf{k}}) - f(\epsilon_{\mu',\mathbf{k}})}{\omega_\lambda - \epsilon_{\mu,\mathbf{k}} - \epsilon_{\mu',\mathbf{k}} + i\eta}$$

$\Longrightarrow$ Red-shift that increases with T_e

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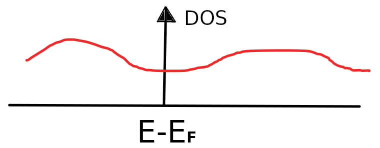

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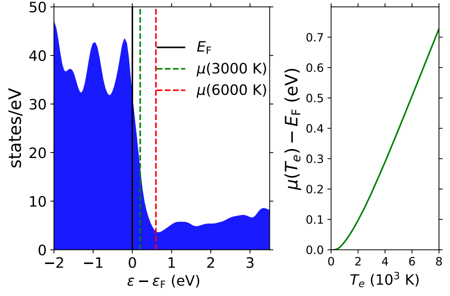
$\Longrightarrow$ Red-shift that increases with T_e

But in the Pd surface...

$$N_e = 2 \int DOS(\epsilon) f(\epsilon, T, \mu) d\epsilon$$

$$f(\epsilon, T, \mu) = \frac{1}{e^{(\epsilon - \mu(T_e)/k_B T} + 1}$$

The chemical potentials shifts to preserve the number of electrons N_e



Where does the blue-shift comes from?

Response function, $\chi(\omega)$

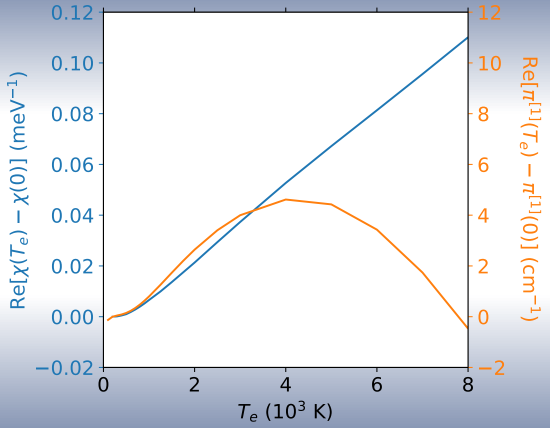
$$\chi(\omega) = \sum_{\mu\mu'\mathbf{k}\sigma} \frac{f(\epsilon_{\mu\mathbf{k}}) - f(\epsilon_{\mu'\mathbf{k}})}{\omega + \epsilon_{\mu\mathbf{k}} - \epsilon_{\mu'\mathbf{k}} + i\eta}.$$

$\Longrightarrow$ electronic structure effects

Phonon self energy, $\pi(\omega)$

$$\pi(\omega) = \sum_{\mu\mu'\mathbf{k}\sigma} |g_{\lambda}^{\mu,\mu'}(\mathbf{k},0)|^2 \frac{f(\epsilon_{\mu\mathbf{k}}) - f(\epsilon_{\mu'\mathbf{k}})}{\omega + \epsilon_{\mu\mathbf{k}} - \epsilon_{\mu'\mathbf{k}} + i\eta}.$$

$\Longrightarrow$ e-ph coupling + electronic structure



Summary

Take home message

- Under thermal heating
- Under **IR pump-probe experiments** conditions the coupling to hot electrons and the EMPPC mechanism compete.
- The **electronic structure of Pd(111) screens the e-ph interaction** giving place to an anomalous blue-shift.
- The **coupling to other phonon modes induces a red-shift**.

eman ta zabal zazu

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Alberto S. Muzas

INSTITUT ZA FIZIKU
@ Zagreb

Dino Novko

Check out our work!

- Phys. Rev. B **107**, L121404 (2023)
- Phys. Rev. B **108**, 045409 (2023)

Thank you!