Anomalous transient blue-shift in the internal stretch mode CO/Pd(111)

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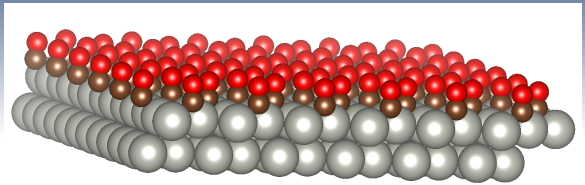
Motivation



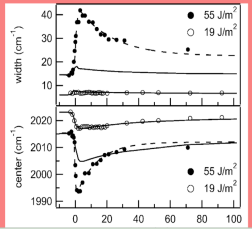
- R. Bombín, A. S. Muzas, D. Novko, J. I. Juaristi, and M. Alducin Phys. Rev. B **107**, L121404 (2023)
- arXiv:2304.10845 **[cond-mat.mtrl-sci]** (2023) (Under revision)

Metallic surfaces covered with polar molecules

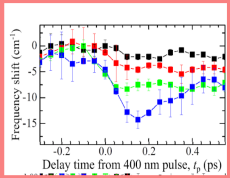
- The internal stretch mode is measured with pump-probe infrared spectroscopy with a resolution of femtoseconds.
- In our case we study the Pd(111) surface with 0.5 ML of CO

Pump-probe experimental results

CO/Ru(0001)

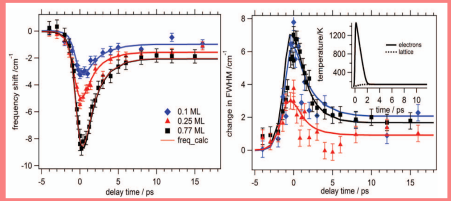


CO/Cu(100)



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

CO/Cu(110)

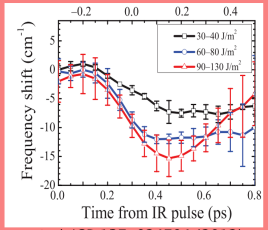


Omiya *et al.* JCP **141**, 214705 (2014)

Always redshift??

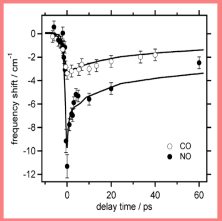
- FCC and HCP Transition metals
- Different surfaces: (111), (100)...
- Different coverages
- Different adsorbates: CO and NO
- Different lasers

CO/Pt(111)



Inoue *et al.* JCP 137, 224704 (2012)

CO and NO on Ir(111)

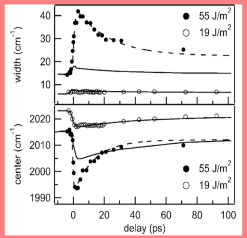


Hamm *et al.* JPC Lett. 1, 1148 (2010)

Anomalous transient blue shift in the initial stage of desorption (111)

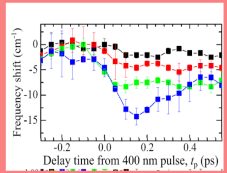
Pump-probe experimental results

CO/Ru(0001)



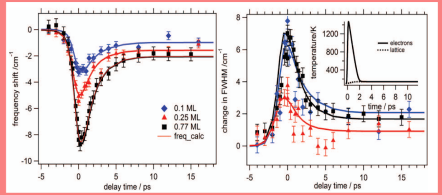
Bonn *et al.* PRL **84** 4653 (2000)

CO/Cu(100)



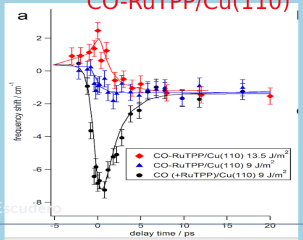
Innoue *et al.* PRL **117,** 186101 (2016)

CO/Cu(110)

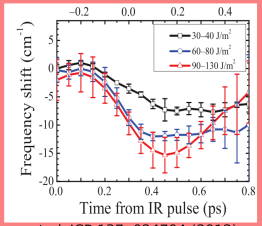


Omiya *et al.* JCP **141**, 214705 (2014)

CO-RuTPP/Cu(110)

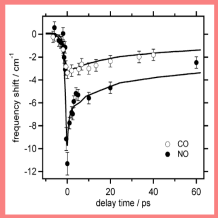


CO/Pt(111)



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

CO and NO on Ir(111)



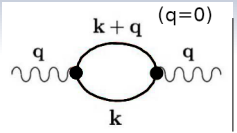
Lane *et al.* JCPC 111, 14198 (2007)

Method

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

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

- interband $\propto g^2$



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

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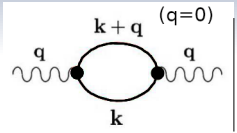
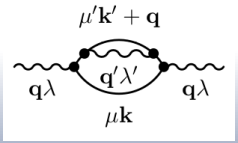


$$\pi_\lambda^{[1]} = \sum_{\mu,\mu',\mathbf{k}} \left| g_\lambda^{\mu,\mu'}(\mathbf{k},0) \right|^2 \frac{f(\epsilon_{\mu,\mathbf{k}}) - f(\epsilon_{\mu',\mathbf{k}})}{\omega_\lambda - \epsilon_{\mu,\mathbf{k}} - \epsilon_{\mu',\mathbf{k}} + i\eta}$$

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



- intraband $\propto g^4$

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

Method

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

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

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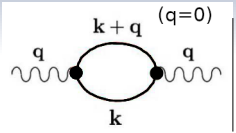

$$\pi_\lambda^{[1]} = \sum_{\mu,\mu',\mathbf{k}} \left| g_\lambda^{\mu,\mu'}(\mathbf{k},0) \right|^2 \frac{f(\epsilon_{\mu,\mathbf{k}}) - f(\epsilon_{\mu',\mathbf{k}})}{\omega_\lambda - \epsilon_{\mu,\mathbf{k}} - \epsilon_{\mu',\mathbf{k}} + i\eta}$$

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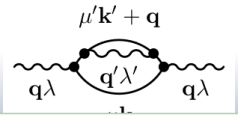

- intraband $\propto g^4$

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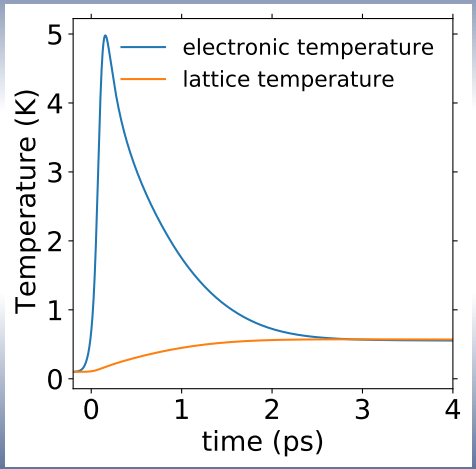
$$+ N^{-1} \sum_{\mathbf{k},\mathbf{q},m,n,\nu} g^{m,n}_{\nu}(\mathbf{k},\mathbf{q}) \hat{c}^{\dagger}_{m,\mathbf{k}+\mathbf{q}} \hat{c}_{n,\mathbf{k}} (\hat{a}_{\nu,\mathbf{q}} +$$

QUANTUMESPRESSO

EPW

Method - time dependence



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

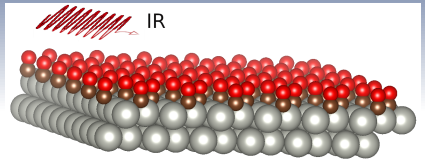
$$C_l \frac{\partial T_l}{\partial t} = G(T_e - T_l),$$

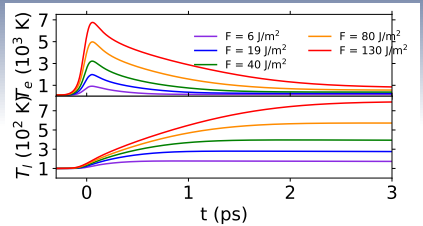
Input parameters

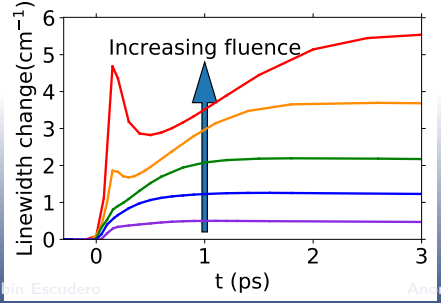
- Heat capacities C_e and C_l.
- thermal conductivity κ_e
- electron-phonon energy exchange coupling constant G

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

CO/Pd(111) - pump-probe experimental conditions







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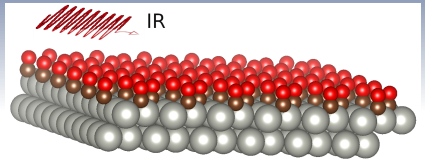

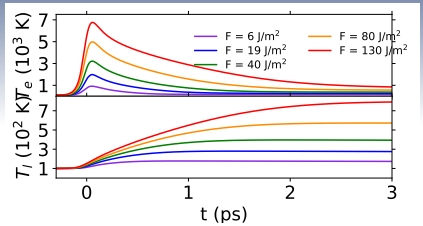

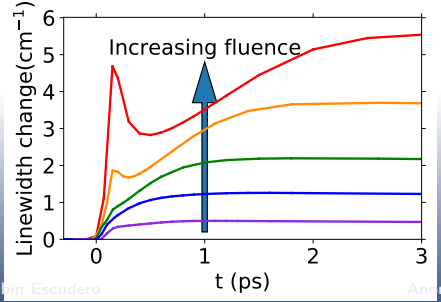

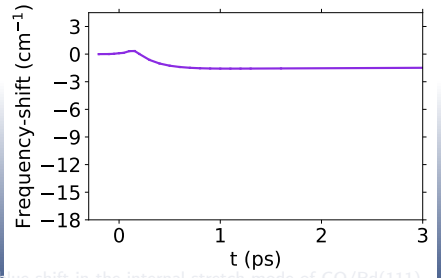

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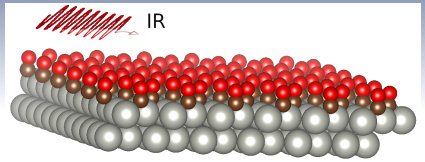
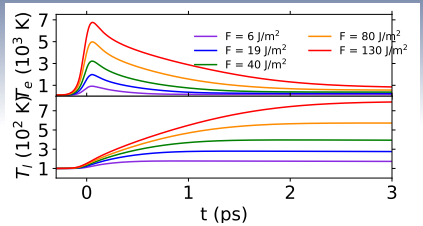
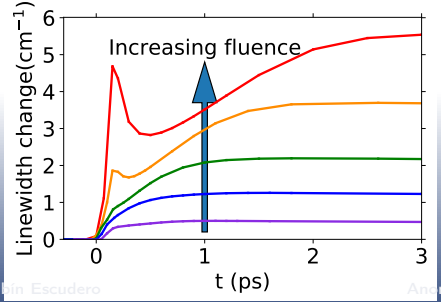
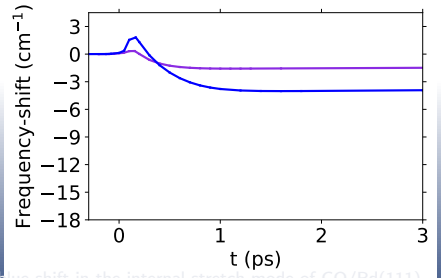
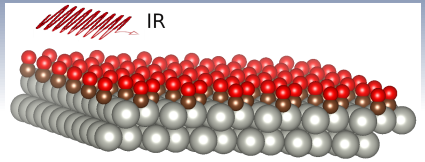


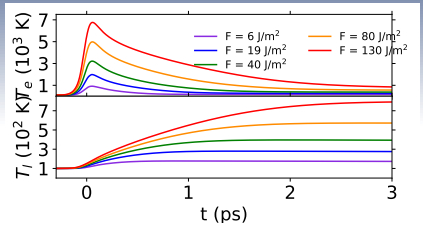


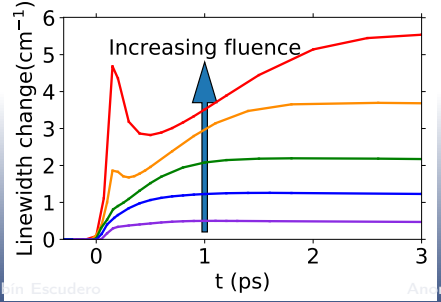


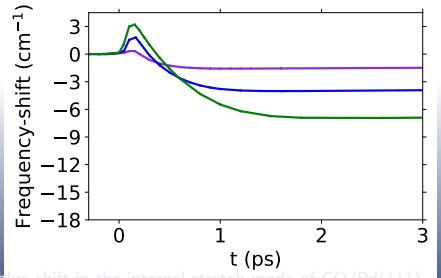


CO/Pd(111) - pump-probe experimental conditions









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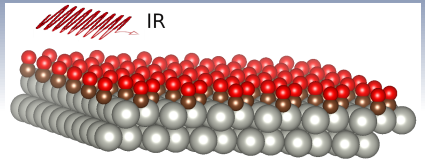

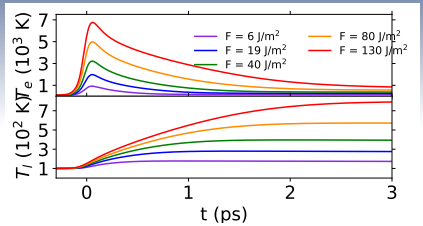

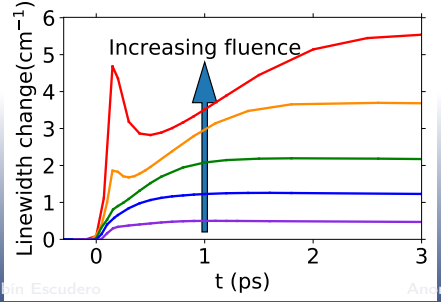

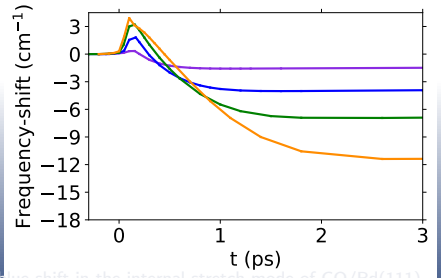

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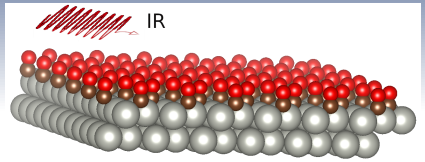
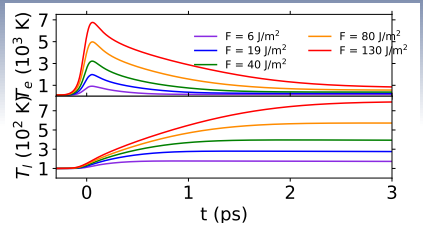
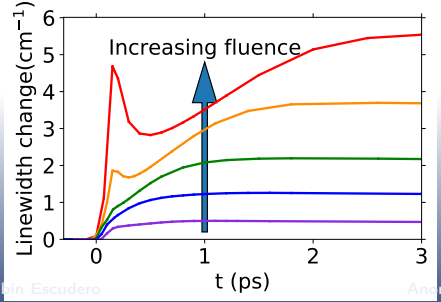
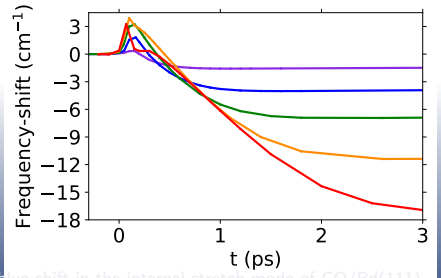
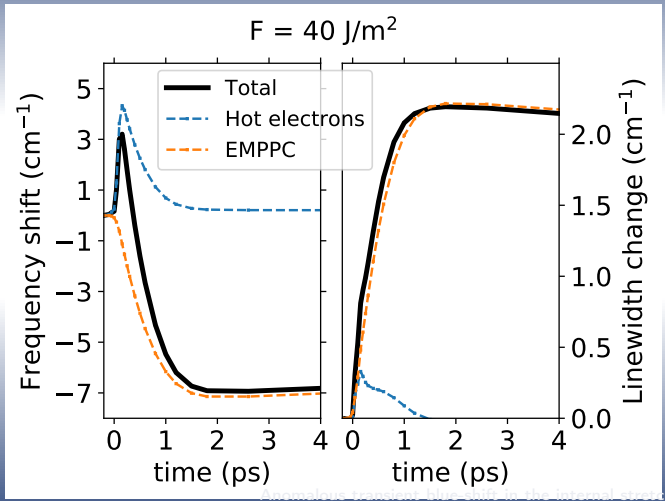






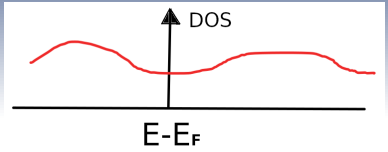


CO/Pd(111) - pump-probe experimental conditions



Time-resolved desorption data shown in the frustrated rotation mode of CO/Pd(111)

Where does the blue-shift comes from?

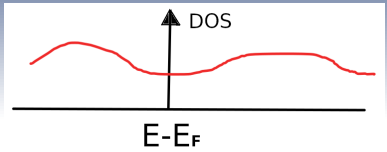


Usually, $\mathrm{Re}[\pi^{[1]}]$ is increased as T_e does

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

$\Longrightarrow$ Red-shift that increases with T_e

Where does the blue-shift comes from?



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

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

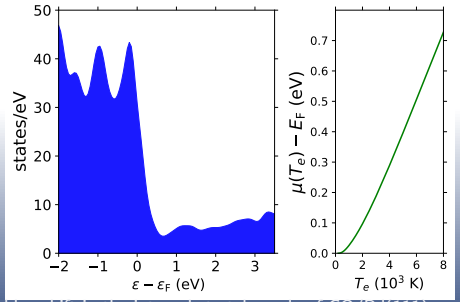
$\Longrightarrow$ Red-shift that increases with T_e

But in the Pd surface...

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

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

The **chemical potentials** shifts to preserve the number of electrons N_e

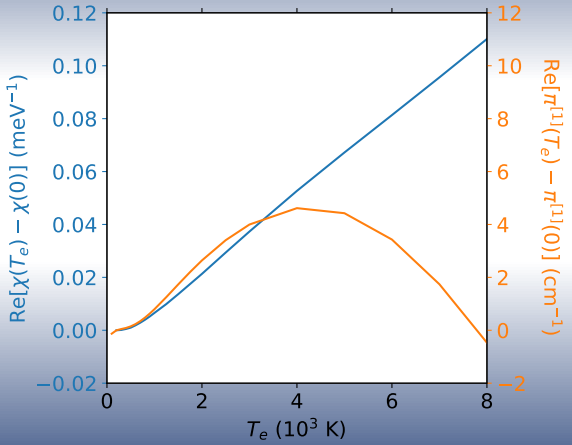


Where does the blue-shift comes from?

the response function, $\chi(\omega)$

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

accounts for the thermal effects that arise from the electronic structure.



Summary

Take home message

- 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**.

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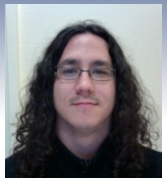

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Check out our work!

- Phys. Rev. B **107**, L121404 (2023)
- arXiv:2304.10845 (2023) (Under revision)

Thank you!