Equilibrium and ultrafast vibrational dynamics from first principles

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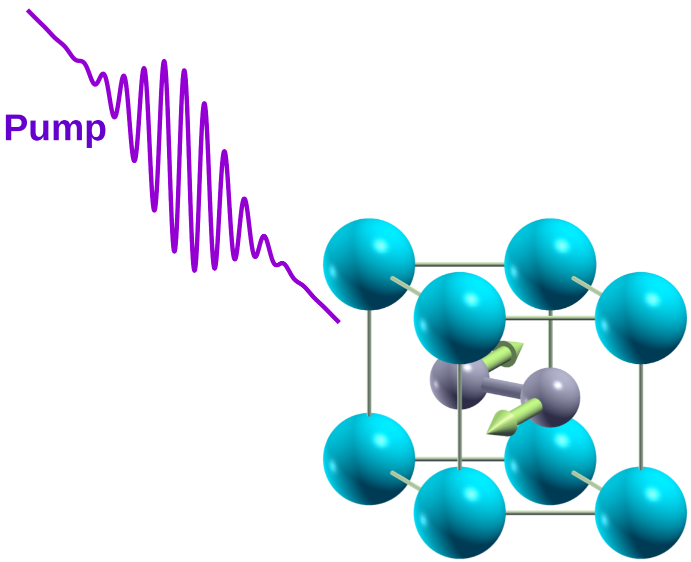
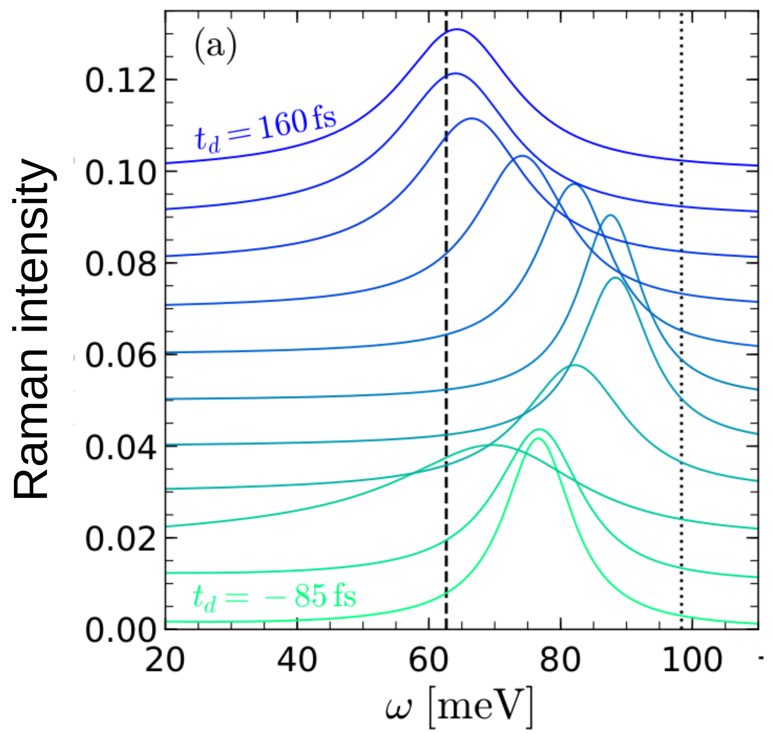
Part I

➔ Ultrafast Raman spectroscopy of MgB_2 – **equilibrium and out-of-equilibrium condition**

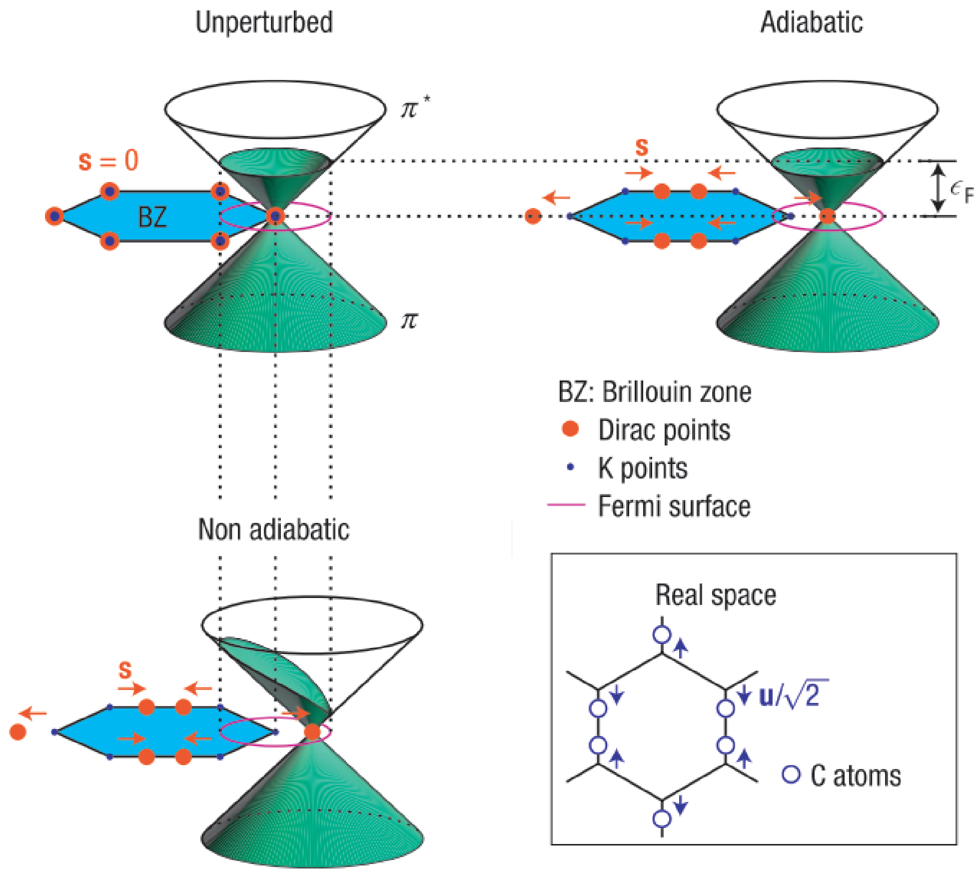




Nonadiabatic effects

- Nonadiabatic – dynamical effects
- well-known examples: graphene/graphite, GIC, carbon nanotubes, MgB_2
- Adiabatic (static) approx. – electrons remain in the instantaneous ground state
- Nonadiabatic (dynamical) approx. – electrons "lag behind" the instantaneous ground state

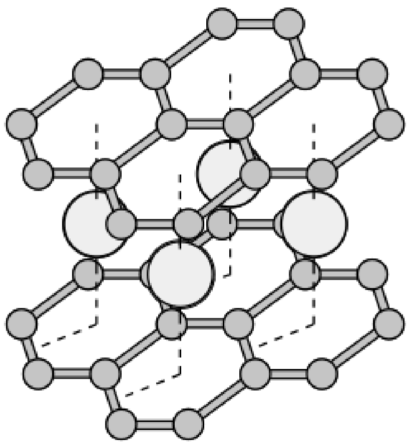
Graphene and E_{2g} phonon

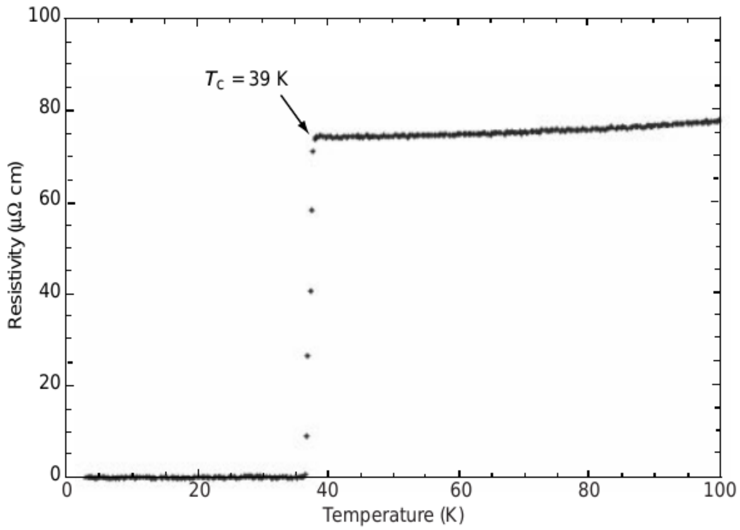


S. Pisana *et al.*, Nature Mater. **6**, 198 2007

MgB_2 - Motivation

- B atoms arranged in hexagonal layered structure
- Superconductive state below T_C = 39 K
- Conventional or unconventional phonon-mediated superconductivity?
- Exp. : $\lambda = 0.6$, T_C = 39 K
  Theory : $\lambda > 0.7$, T_C > 50 K
- Anharmonicity? Nonadiabatic superconductivity? … ?

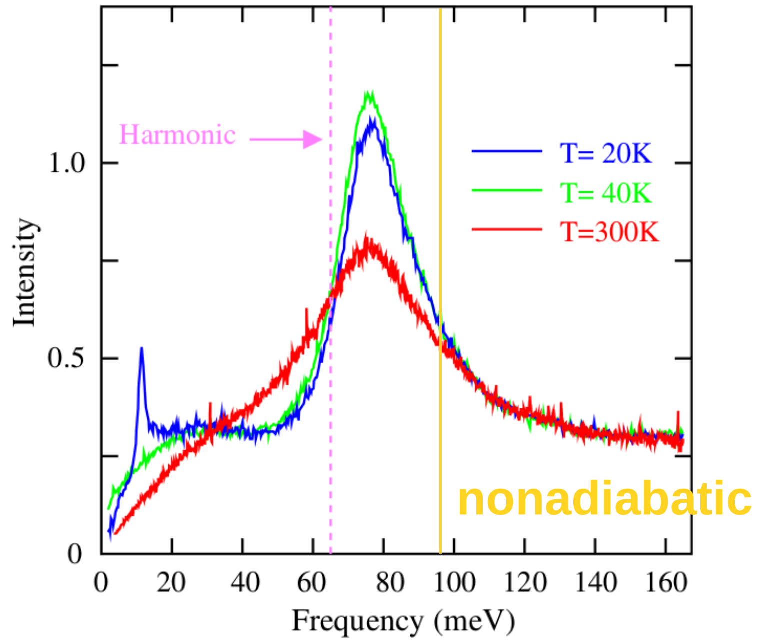




J. Nagamatsu *et al.*, Nature **410**, 63 2001)

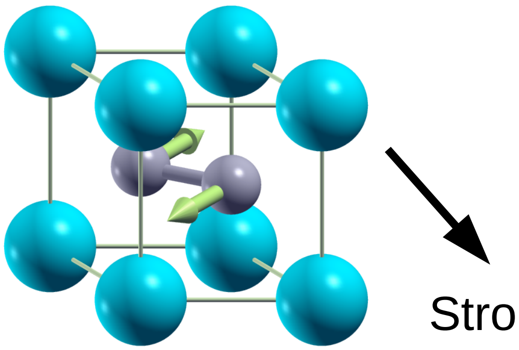
MgB_2 - Motivation

- Strong EPC between E_{2g} mode and σ electrons
- Anomalous Raman spectrum for E_{2g} mode – adiabatic and nonadiabatic theory fail
- Temperature dependence and large broadening of E_{2g} mode – anharmonicity?



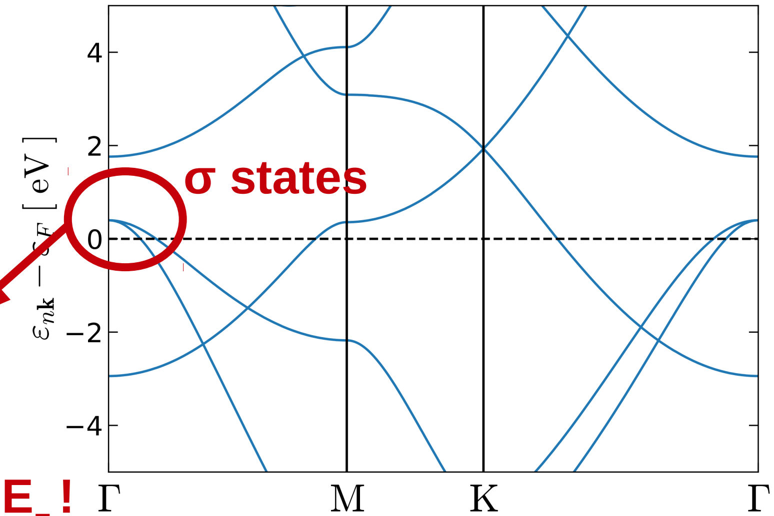
J. W. Quilty *et al.*, PRL **88**, 087001 (2002)

E_{2g} phonon mode



Strong EPC !

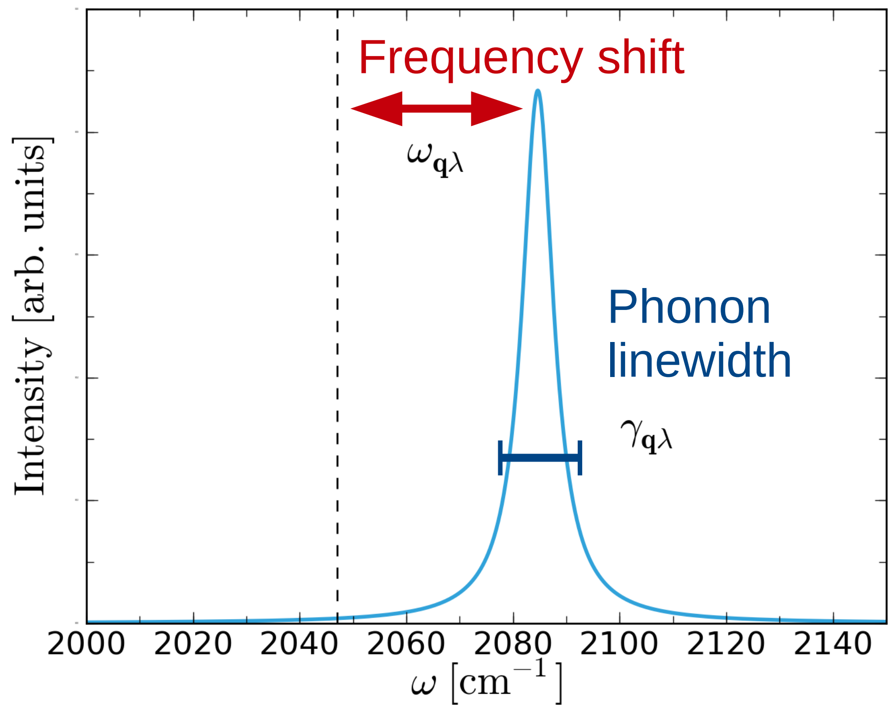
Small E_F !



Phonon self-energy

- Understanding the relaxation processes of vibrating molecules on metal surfaces
- **Phonon self-energy using many body perturbation theory**

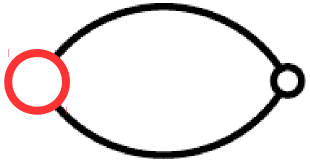
➔ Phonon linewidth and frequency renormalization due to electron-phonon coupling



$$\gamma_{\mathbf{q}\lambda} = -2\mathrm{Im}\Pi_\lambda(\mathbf{q}, \omega_{\mathbf{q}\lambda})$$

$$\omega^2 = \omega_{\mathbf{q}\lambda}^2 + 2\omega_{\mathbf{q}\lambda}\mathrm{Re}\Pi_\lambda(\mathbf{q}, \omega)$$

$$\Pi_\lambda(\omega) = \Pi_\lambda^{\mathrm{intra}}(\omega) + \Pi_\lambda^{\mathrm{inter}}(\omega)$$



Phonon self-energy

- Understanding the relaxation processes of vibrating molecules on metal surfaces
- **Phonon self-energy using many body perturbation theory**

  ➔ Phonon linewidth and frequency renormalization due to electron-phonon coupling

- Dynamical matrix

$$\mathcal{D}(\omega) = \sum_{\mu\mu'\mathbf{k}} \frac{(f_{\mu\mathbf{k}} - f_{\mu'\mathbf{k}}) d^*_{\mu\mu',\nu}(\mathbf{k},0,\omega) d^b_{\mu\mu',\nu}(\mathbf{k},0)}{\omega + i\eta + \varepsilon_{\mu\mathbf{k}} - \varepsilon_{\mu'\mathbf{k}}} + \int d\mathbf{r} n(\mathbf{r}) \Delta^2 V_{\text{ion}}(\mathbf{r})$$

Phonon self-energy contribution

Bare (ionic) contribution

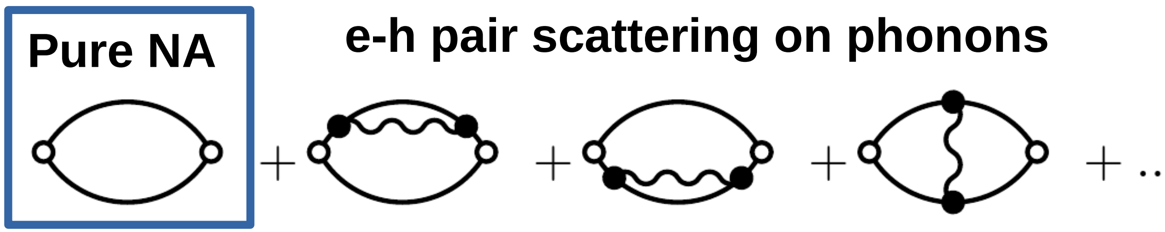
➔ Adiabatic contribution:

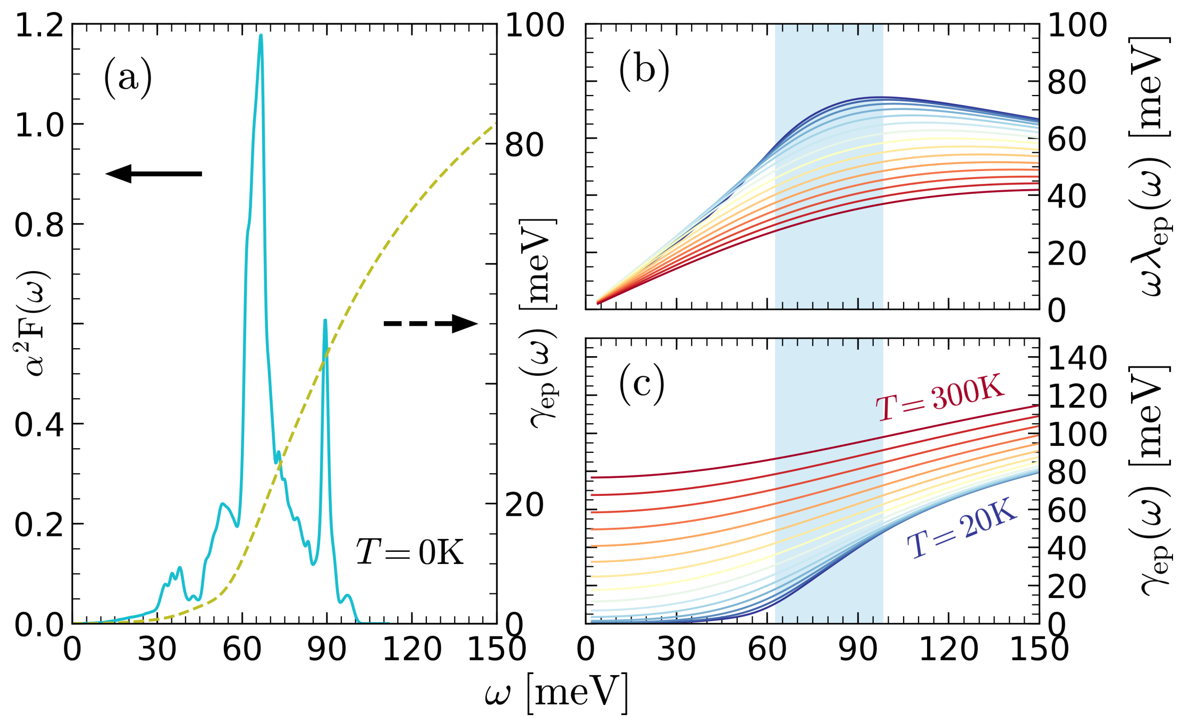
$$\omega_{\text{A}}^2 = \mathcal{D}(0)/M$$

Electron-hole pair scattering on phonons

- Eliashberg function – λ = 0.6

- Electron-hole pair lifetime and energy renormalization effects – $\gamma_{ep}(\omega)$ and $\omega\lambda_{ep}(\omega)$





Pure NA

$$\pi_\nu^{0,\mathrm{intra}}(\omega) = \sum_{\mu\mathbf{k}} \left|g_\nu^{\mu\mu}(\mathbf{k},0)\right|^2 \left[-\frac{\partial f(\varepsilon_{\mu\mathbf{k}})}{\partial \varepsilon_{\mu\mathbf{k}}}\right]$$

NA with e-h pair scattering

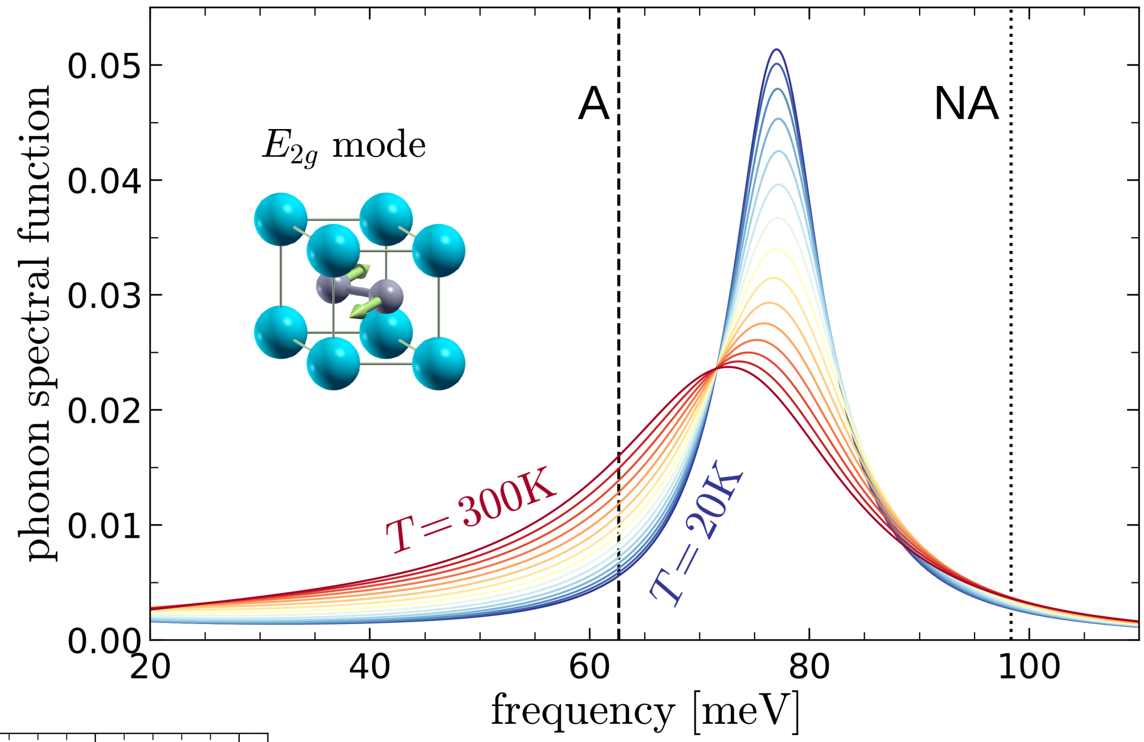
$$\pi_\nu^{\mathrm{intra}}(\omega) = \sum_{\mu\mathbf{k}} \left|g_\nu^{\mu\mu}(\mathbf{k},0)\right|^2 \left[-\frac{\partial f(\varepsilon_{\mu\mathbf{k}})}{\partial \varepsilon_{\mu\mathbf{k}}}\right] \times \frac{\omega}{\omega[1+\lambda_n(\omega)] + i/\tau_n(\omega)}.$$

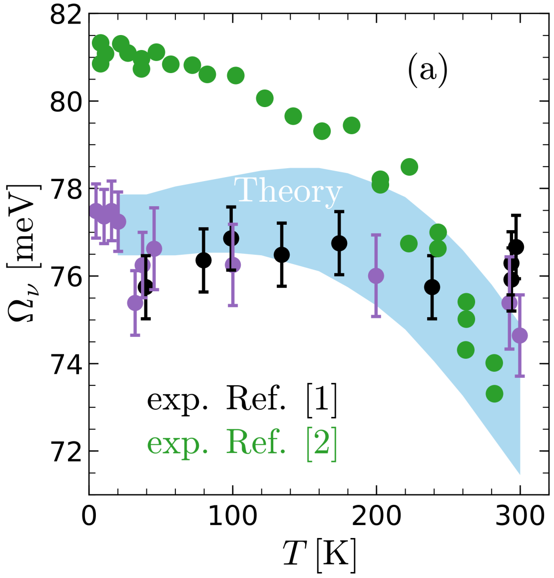
E. Cappelluti PRB **73**, 140505(R) (2006)

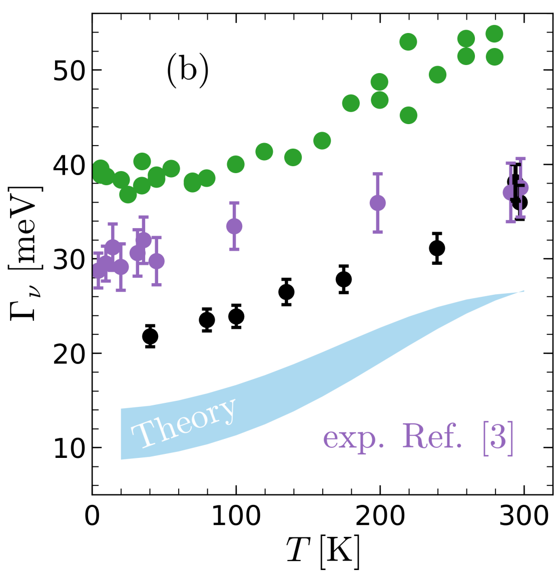
D. Novko, PRB **98**, 041112(R) (2018)

Frequency and linewidth of E_{2g} mode

- Phonon spectral function of the E_{2g} mode
- Strong temperature dependence of phonon frequency and linewidth
- Good agreement with the Raman measurements







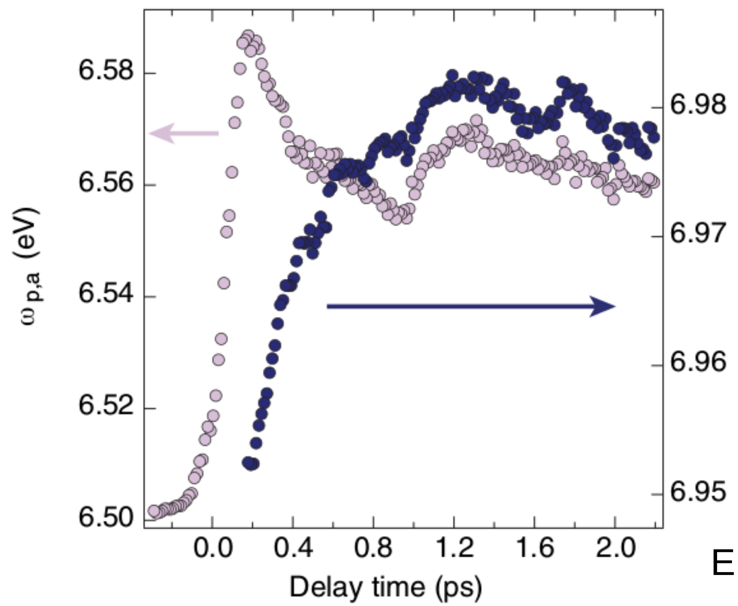
[1] Yu. S. Ponosov and S. V. Streltsov PRB **96**, 214503 (2017)

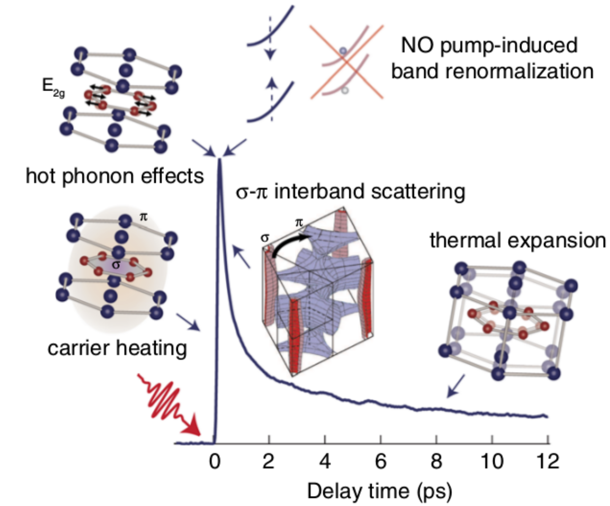
[2] M. d'Astuto *et al.*, PRB **75**, 174508 (2007)

[3] P. M. Rafailov, M.Dworzak, and C. Thomsen, Solid State Commun. **122** 455 (2002)

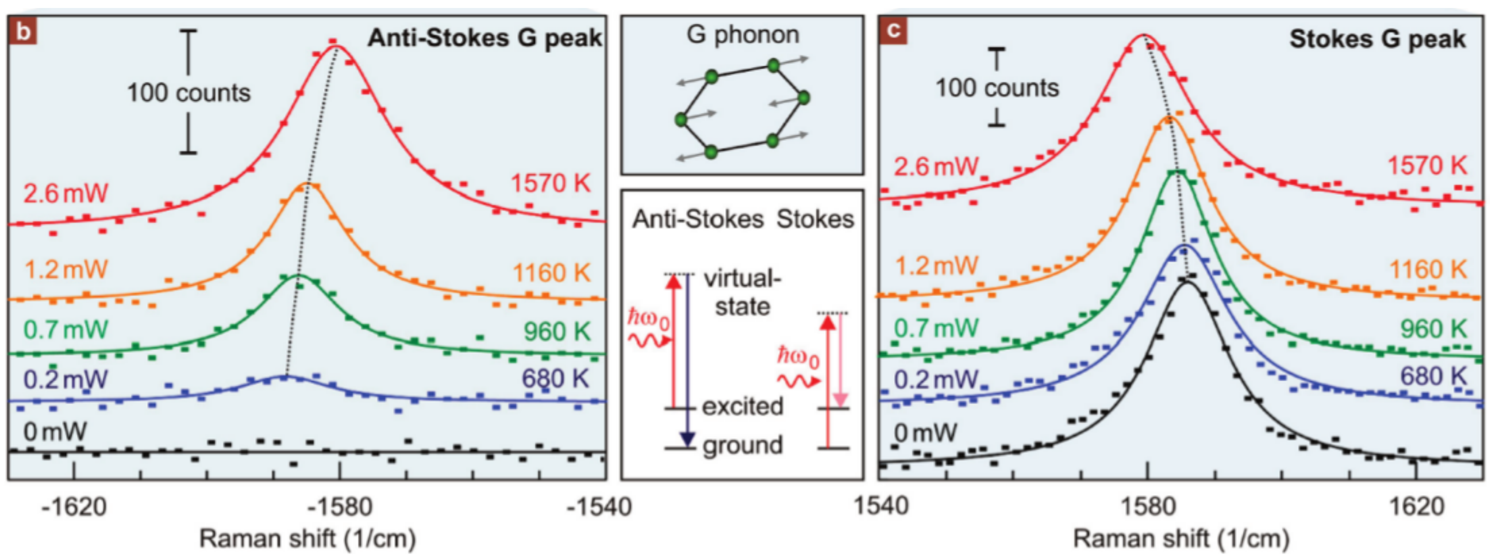
Transient response - Motivation

- Transient reflectivity measurements – hot E_{2g} phonon scenario
- In analogy with the hot G phonon in graphene





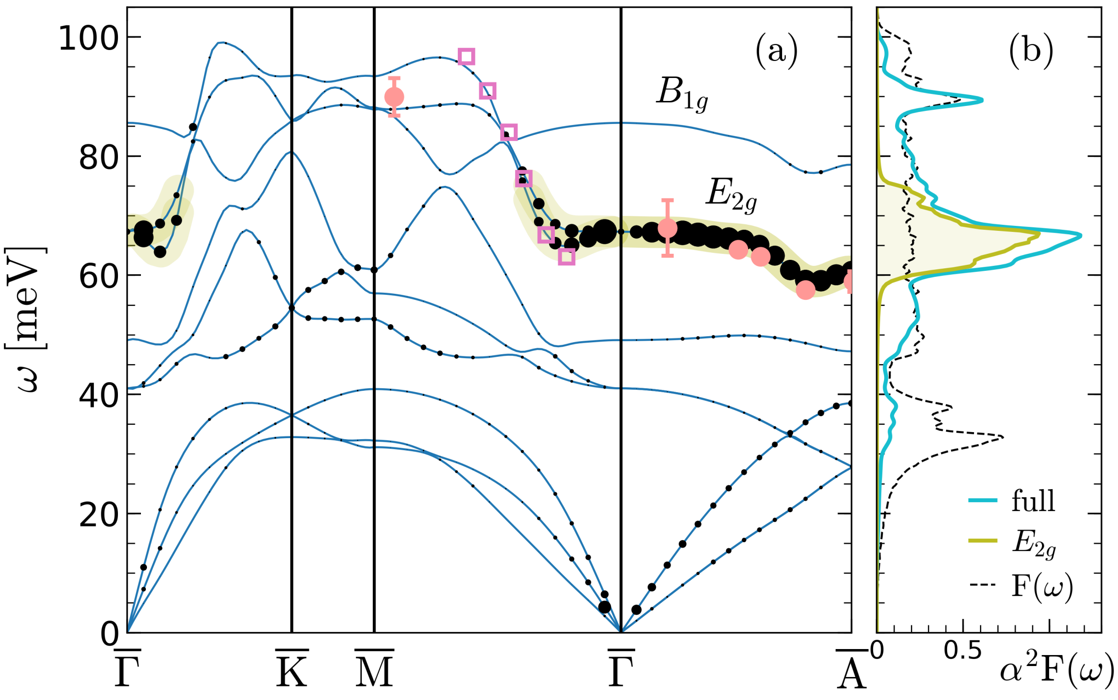
E. Baldini *et al*., PRL **119**, 097002 (2017)



D.-H. Chae *et al*., Nano Lett., **10**, 466 (2010)

Hot phonons in MgB_2

- EPC strength λ along symmetry points (size of black circles)
- Total λ = 0.6 – good agreement with the experiments
- Hot phonons: E_{2g} modes around Γ and along Γ-A path of 1BZ
- λ_{hot} = 0.32



Exp: purple and red points

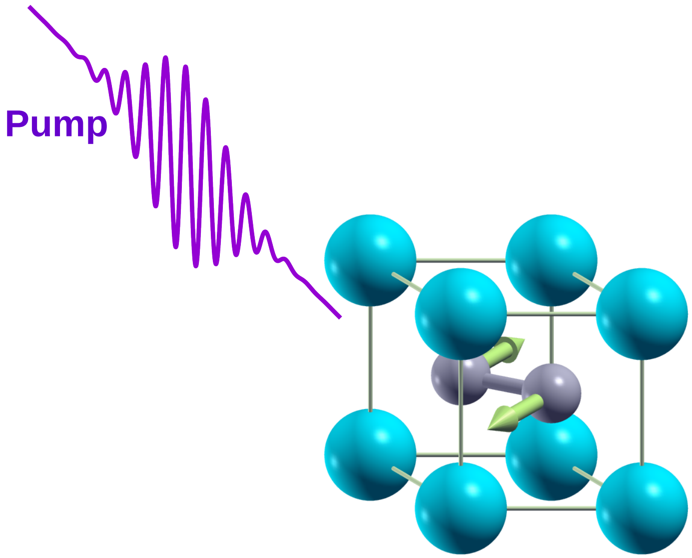
A.Q.R. Baron *et al*., PRL **92**, 197004 (2004)

A. Shukla *et al*., PRL **90**, 095506 (2003)

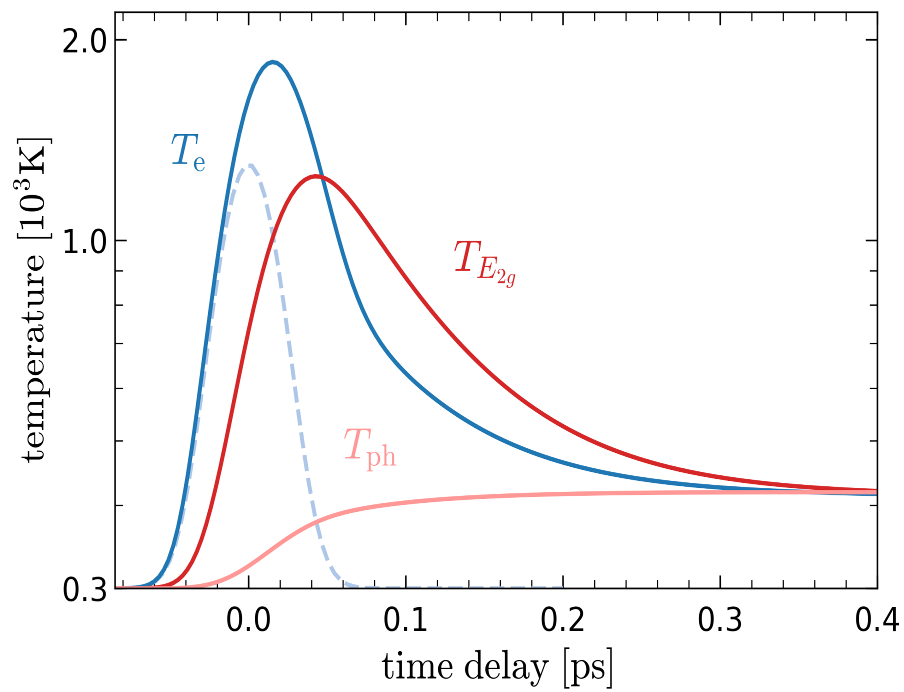
- Pure **anisotropy** of the EPC - different hot phonon scenario than in graphene-based systems and semiconductors (reduced phase space)

Transient response

- Three subsystems - electrons, hot E_{2g} phonons, and remnant cold modes



- Three temperature model – electrons T_e, hot phonons T_{E2g}, and T_{ph}

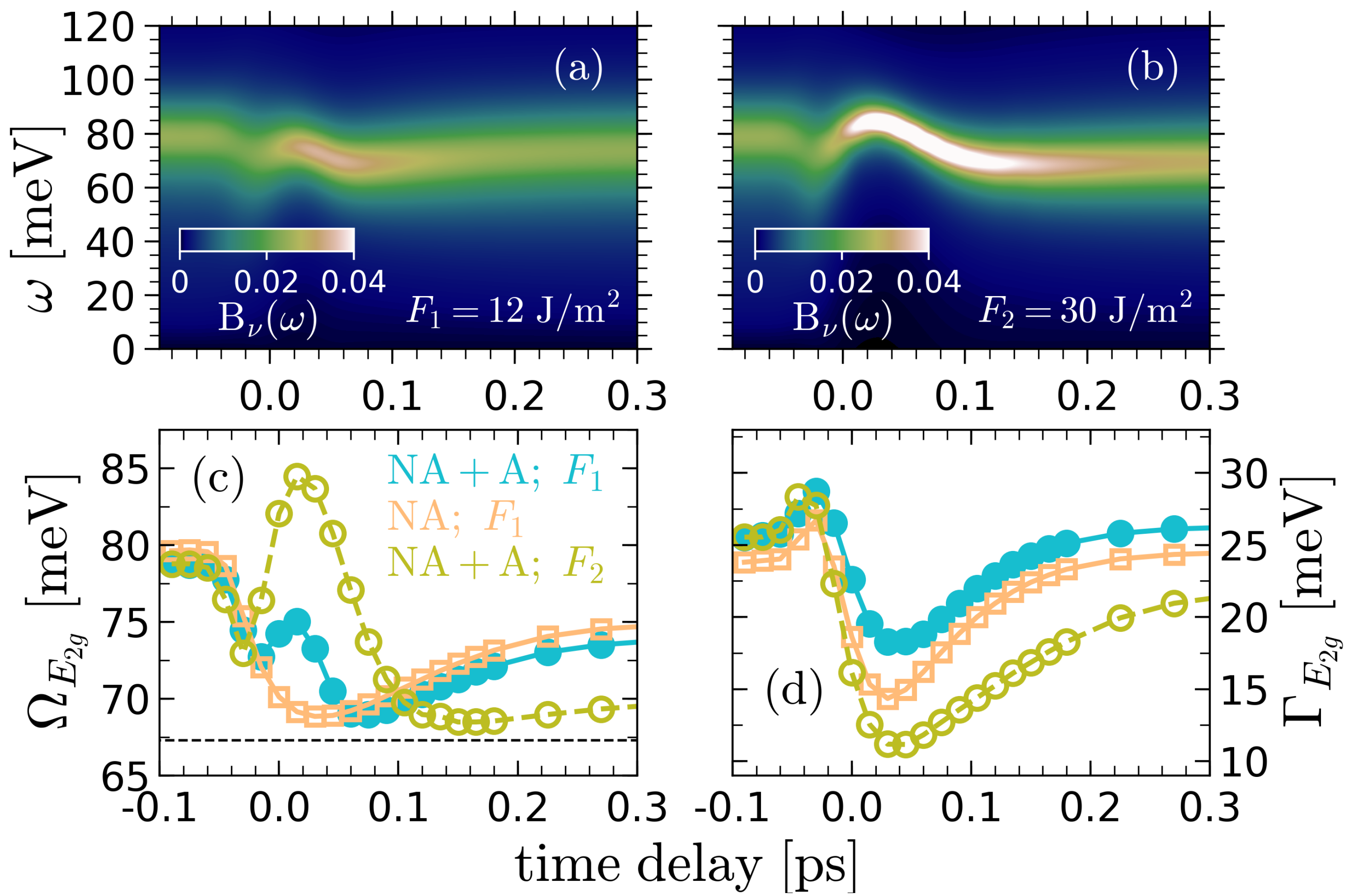


$$C_e \frac{\partial T_e}{\partial t} = S(z,t) + \nabla_z(\kappa \nabla_z T_e) - G_{E_{2g}}(T_e - T_{E_{2g}}) - G_{ph}(T_e - T_{ph}),$$

$$C_{E_{2g}} \frac{\partial T_{E_{2g}}}{\partial t} = G_{E_{2g}}(T_e - T_{E_{2g}}) - C_{E_{2g}} \frac{T_{E_{2g}} - T_{ph}}{\tau_0},$$

$$C_{ph} \frac{\partial T_{ph}}{\partial t} = G_{ph}(T_e - T_{ph}) + C_{E_{2g}} \frac{T_{E_{2g}} - T_{ph}}{\tau_0}.$$

Transient response



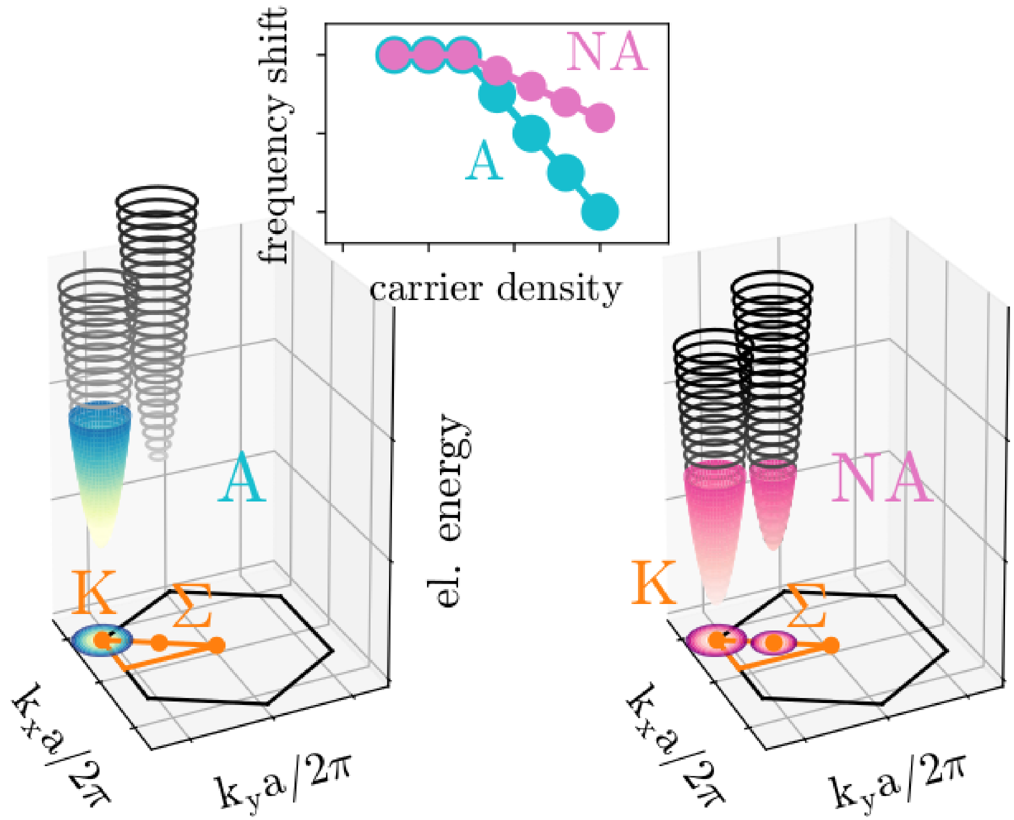
- Ultrafast Raman spectroscopy of MgB_2
- Frequency change – competition between **redshift** and **blueshift**

Nonadiabatic contribution, dependent on T_{E2g}

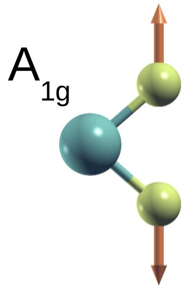
Adiabatic contribution, dependent on T_e

Part II

➔ Breakdown of adiabaticity in doped single-layer transition metal dichalcogenides



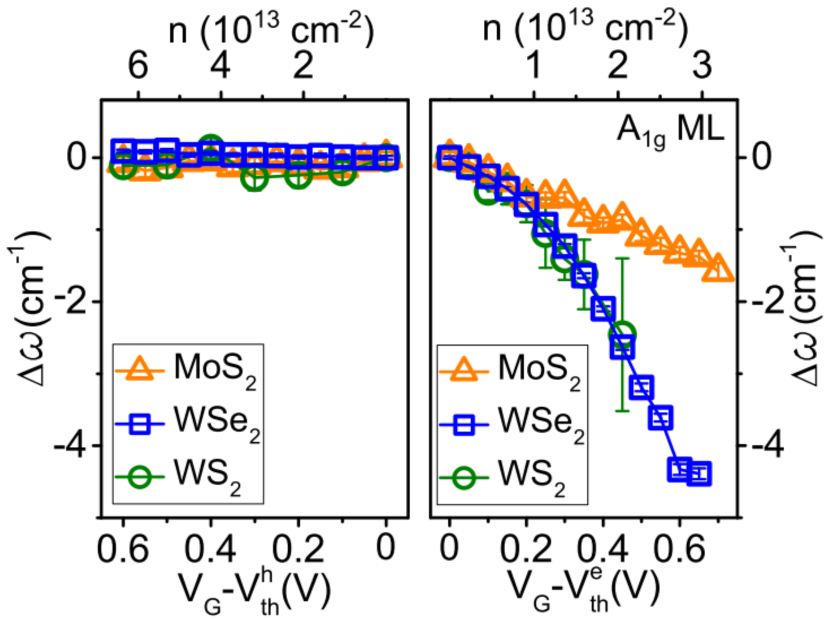
Motivation

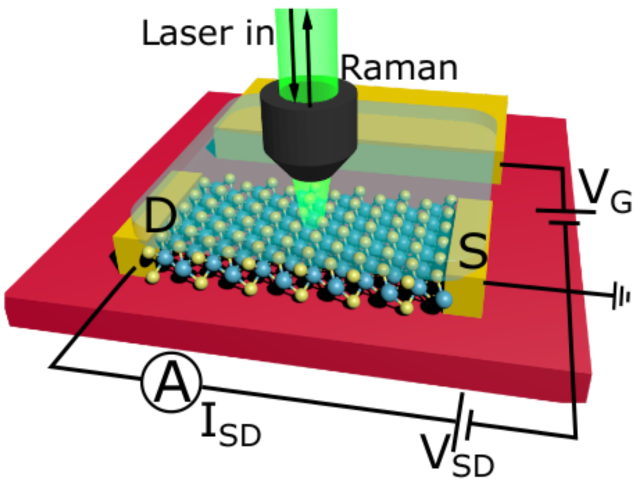


- Raman spectroscopy of single-layer TMD transistors

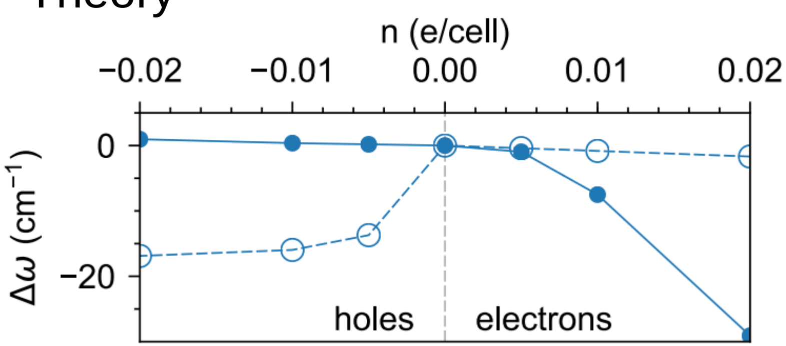
- Adiabatic DFT largely overestimates the experimental Raman shifts

EXP.





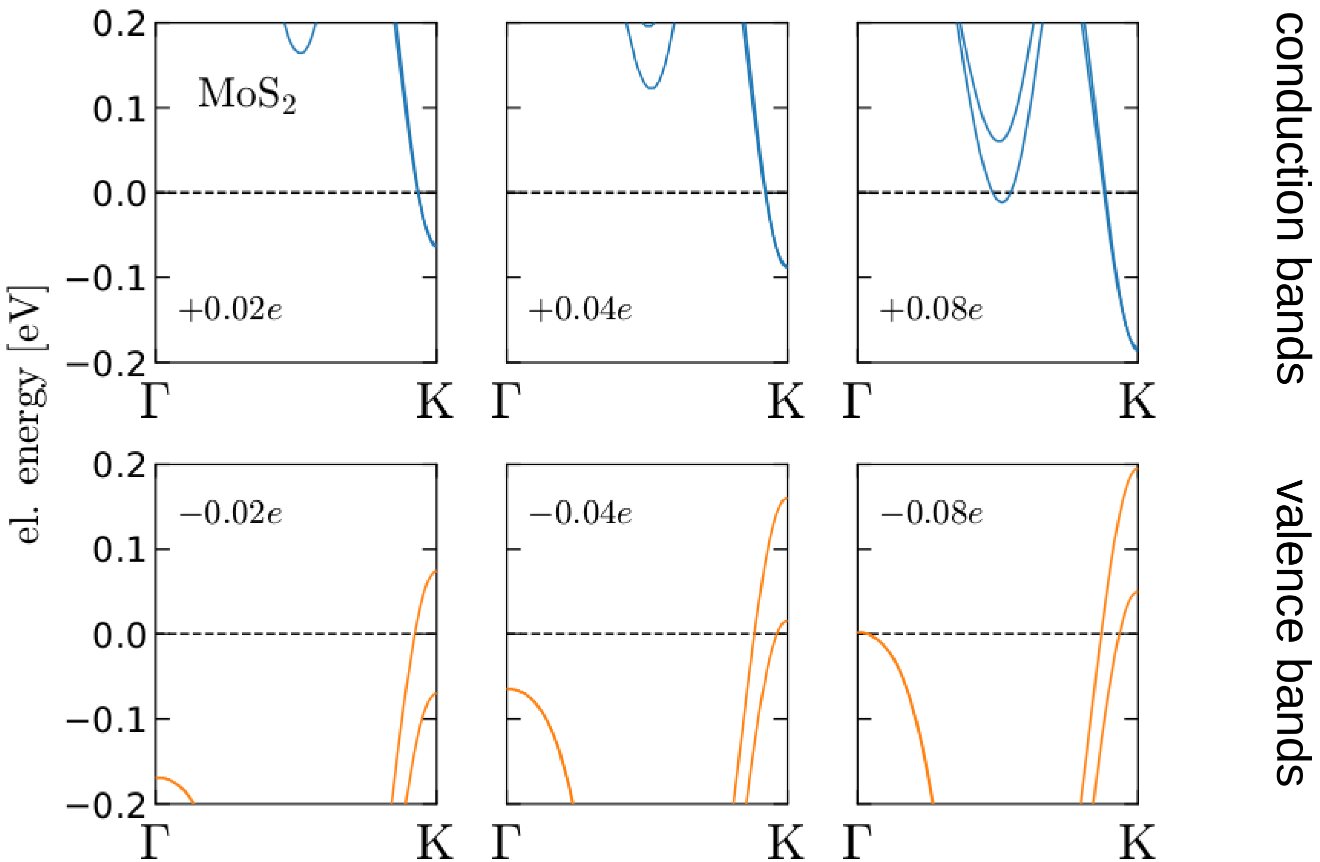
Theory



T. Sohier *et al.*, Phys. Rev. X **9**, 031019 (2019)

Electronic band structure

➔ multiple valleys in both valence and conduction bands



Electronic band structure

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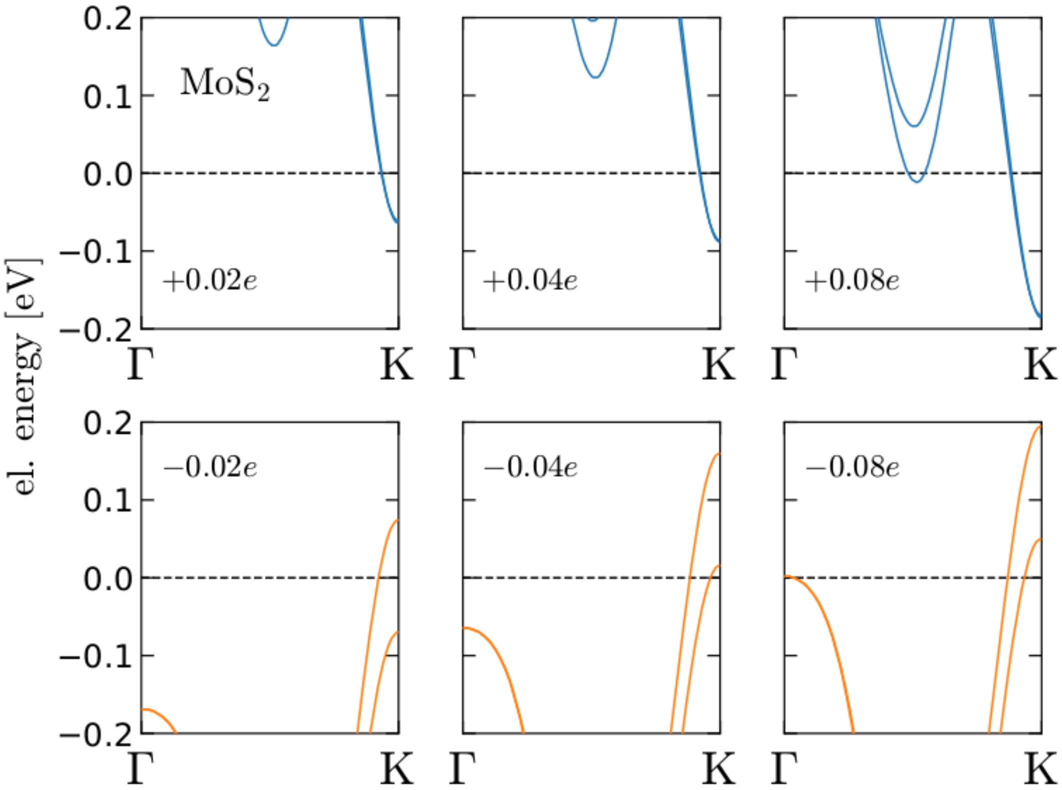
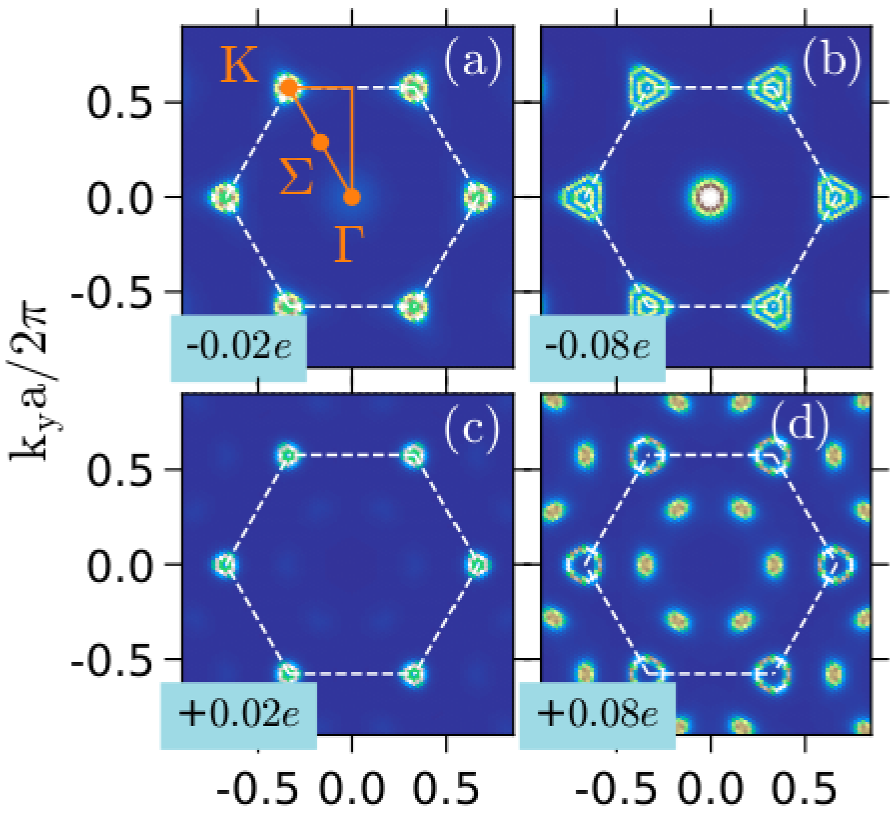


MoS_2 Fermi surface

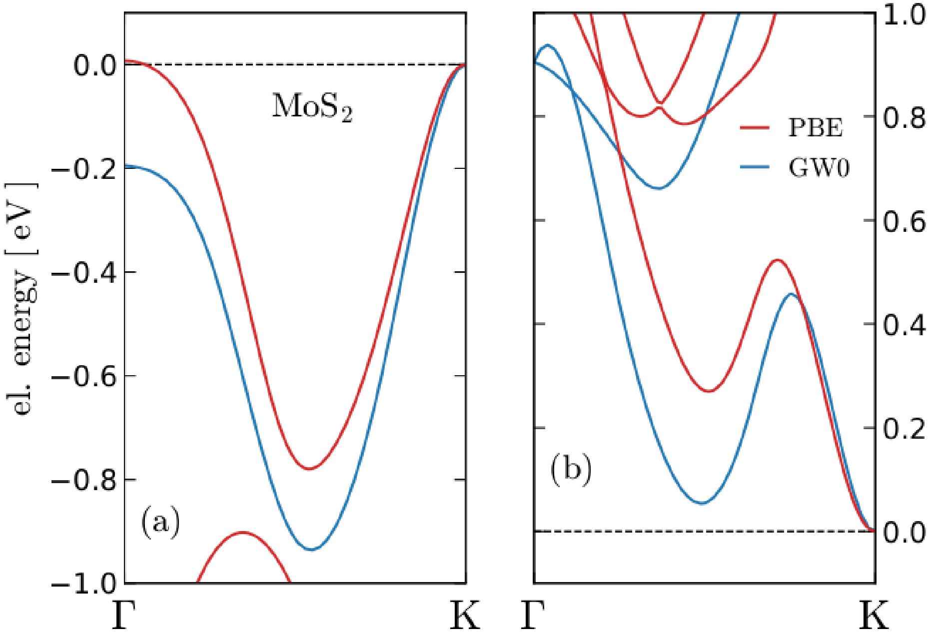


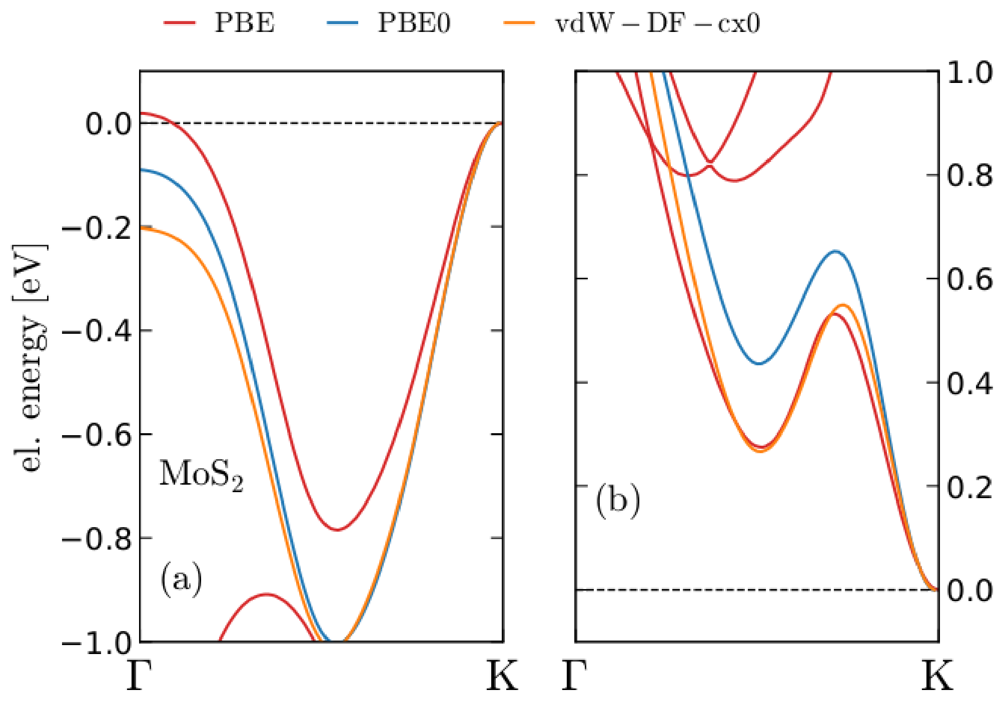
e^-/h^+ doped system

➔ doping-induced **Lifshitz transitions**

Electronic band structure

- PBE xc functional fails to reproduce the correct band structure of TMDs – band gap + **topology of valleys**

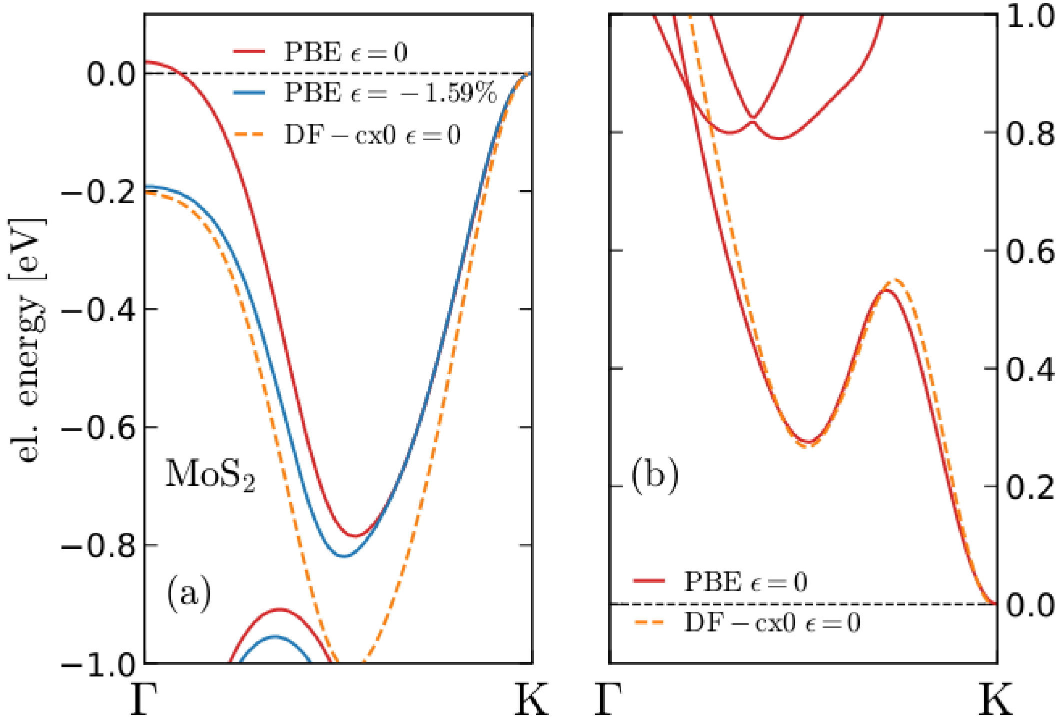


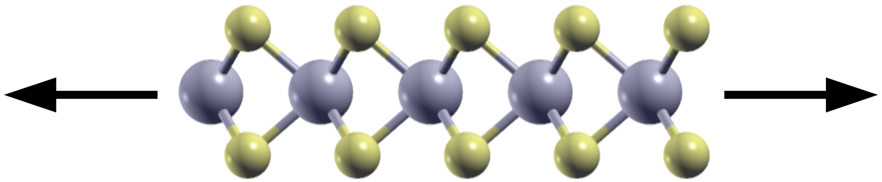


- importance of **non-local electron-electron interaction** – determines the onset of Lifshitz transition

Electronic band structure

➔ PBE with strain in order to get the **right topology of valleys**





Raman spectra

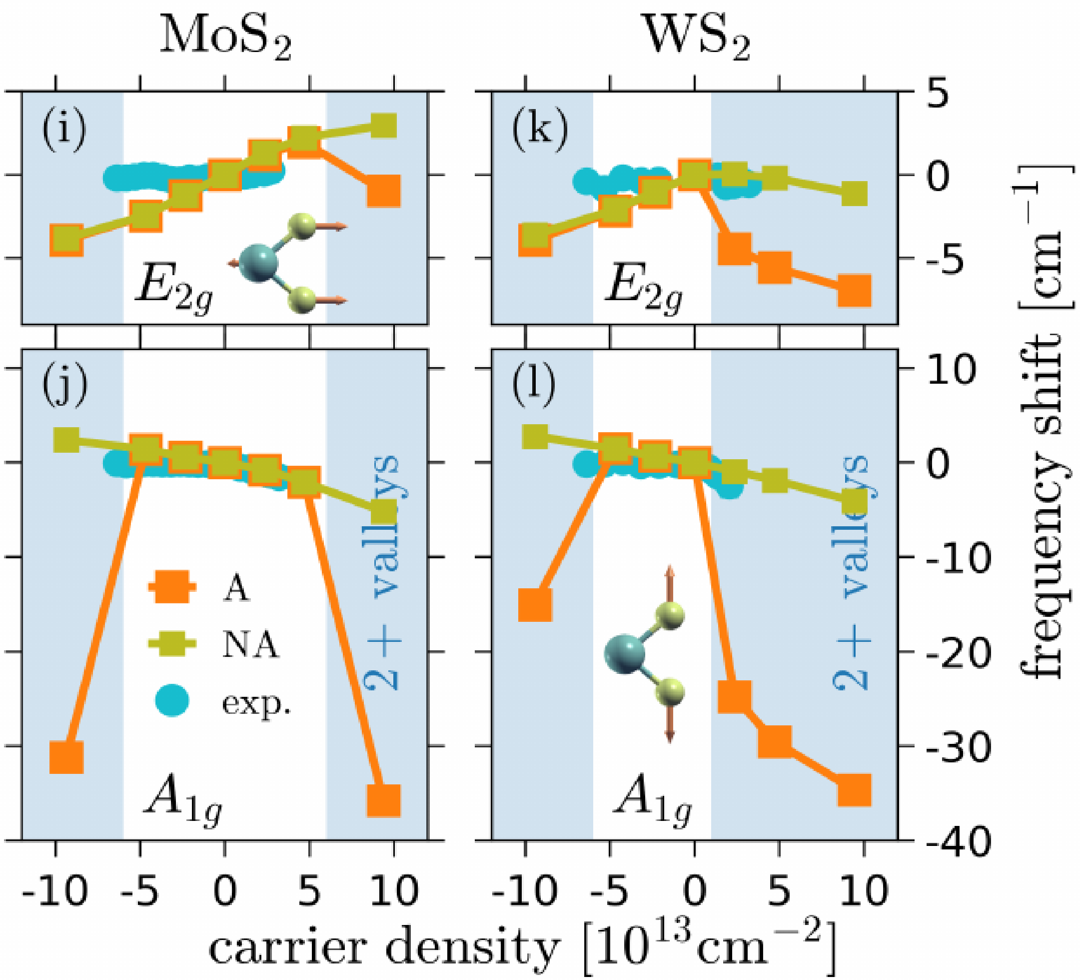
➔ Frequency shifts of A_{1g} and E_{2g} phonon modes as a function doping

➔ **strong NA renormalization of frequencies** when both valleys are partially occupied/empty – $\Delta\omega = 30\ cm^{-1}$

➔ 2 regimes:

(i) **adiabatic** region where only 1 valence/conduction band is slightly empty/filled

(ii) **nonadiabatic** region where 2 valleys intersect the Fermi energy



exp. : T. Sohier *et al*., Phys. Rev. X **9**, 031019 (2019)

NA effects – comparison

- Strength of the NA effects in comparison to other systems

System	$\Delta\omega_{ph}/\omega_{ph}$
TMDs FET	8%
Graphene FET	3%
Graphite Intercalation compounds (LiC_6)	16%
MgB_2	46%

2D

3D

Graphene : M. Lazzeri and F. Mauri, PRL 97 266407 (2006)

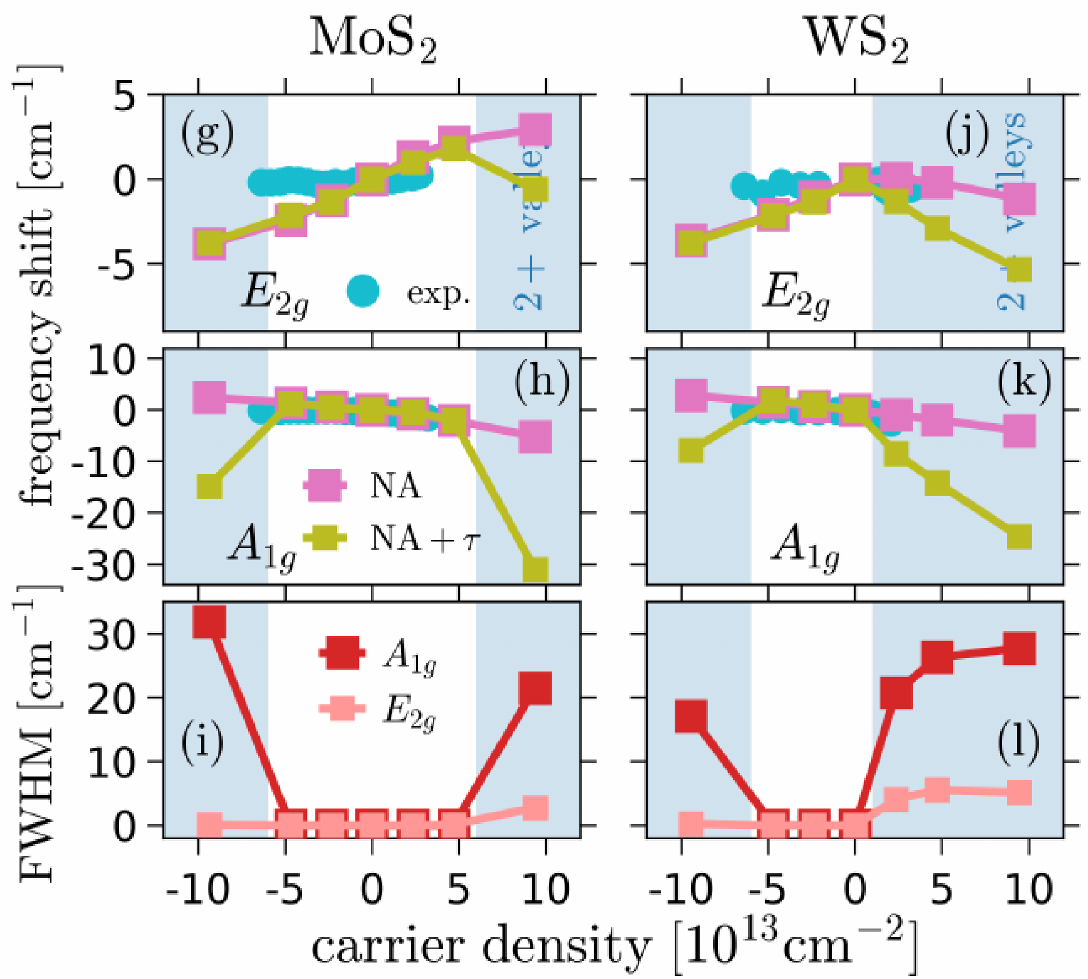
GIC : A. M. Saitta et al., PRL 100 226401 (2008)

Raman spectra

- Frequency shifts of A_{1g} and E_{2g} phonon modes as a function doping

- **Strong NA + strong e-h scattering (due to el-ph coupling)** when both valleys are partially occupied/empty

$$\pi_\nu^{\mathrm{intra}}(\omega) = \sum_{\mu\mathbf{k}} \left|g_\nu^{\mu\mu}(\mathbf{k},0)\right|^2 \left[-\frac{\partial f(\varepsilon_{\mu\mathbf{k}})}{\partial \varepsilon_{\mu\mathbf{k}}}\right] \times \frac{\omega}{\omega[1+\lambda_n(\omega)] + i/\tau_n(\omega)}.$$

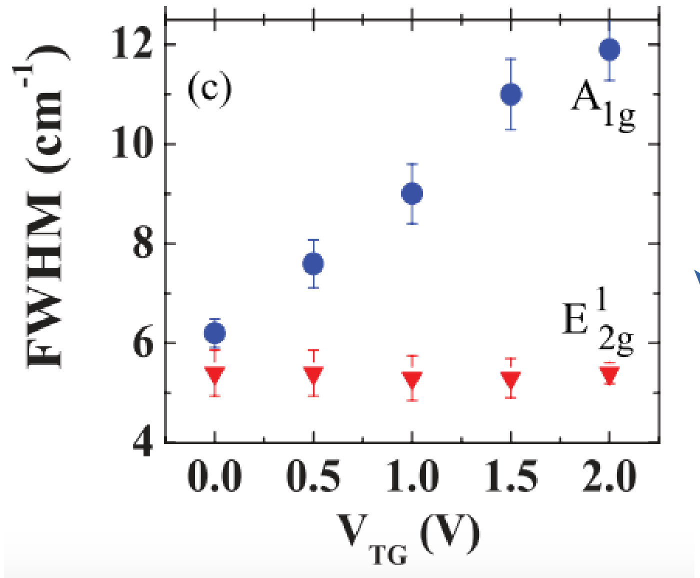


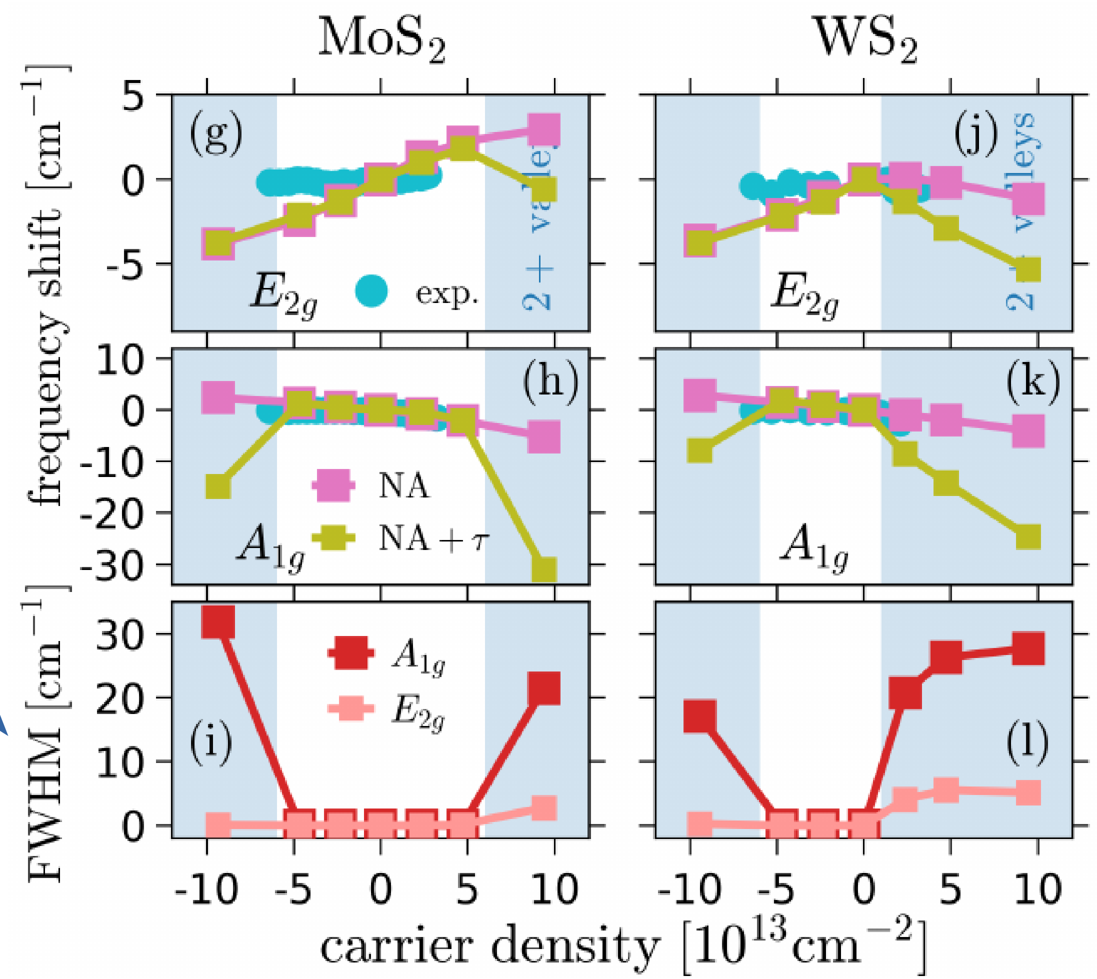
exp. : T. Sohier *et al*., Phys. Rev. X **9**, 031019 (2019)

Raman spectra

- Frequency shifts of A_{1g} and E_{2g} phonon modes as a function doping

- **strong e-h scattering due to el-ph coupling –** induces phonon broadening



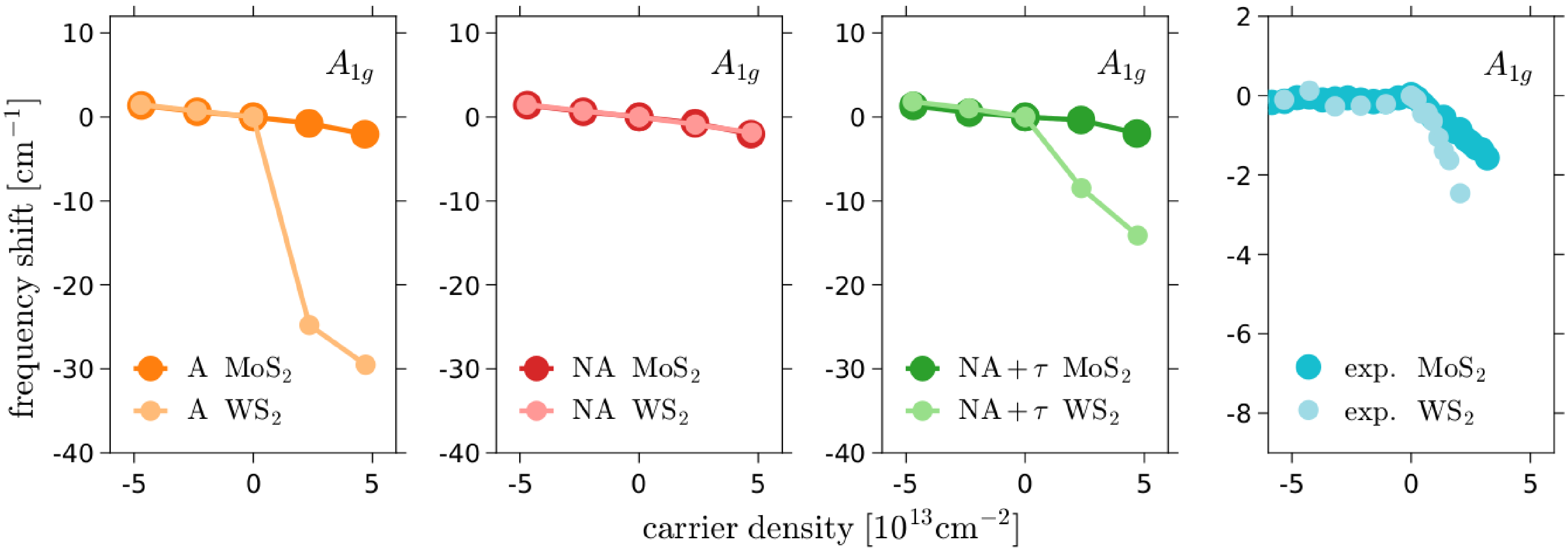


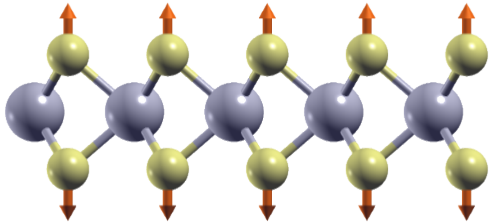
B. Chakraborty *et al.*, PRB **85**, 161403(R) (2012)

- FWHM(A_{1g}) >> FWHM(E_{2g})

Raman spectra

➔ Summary – the effect of **nonadiabatic** el-ph coupling





Raman spectra - summary

- 2 regimes:

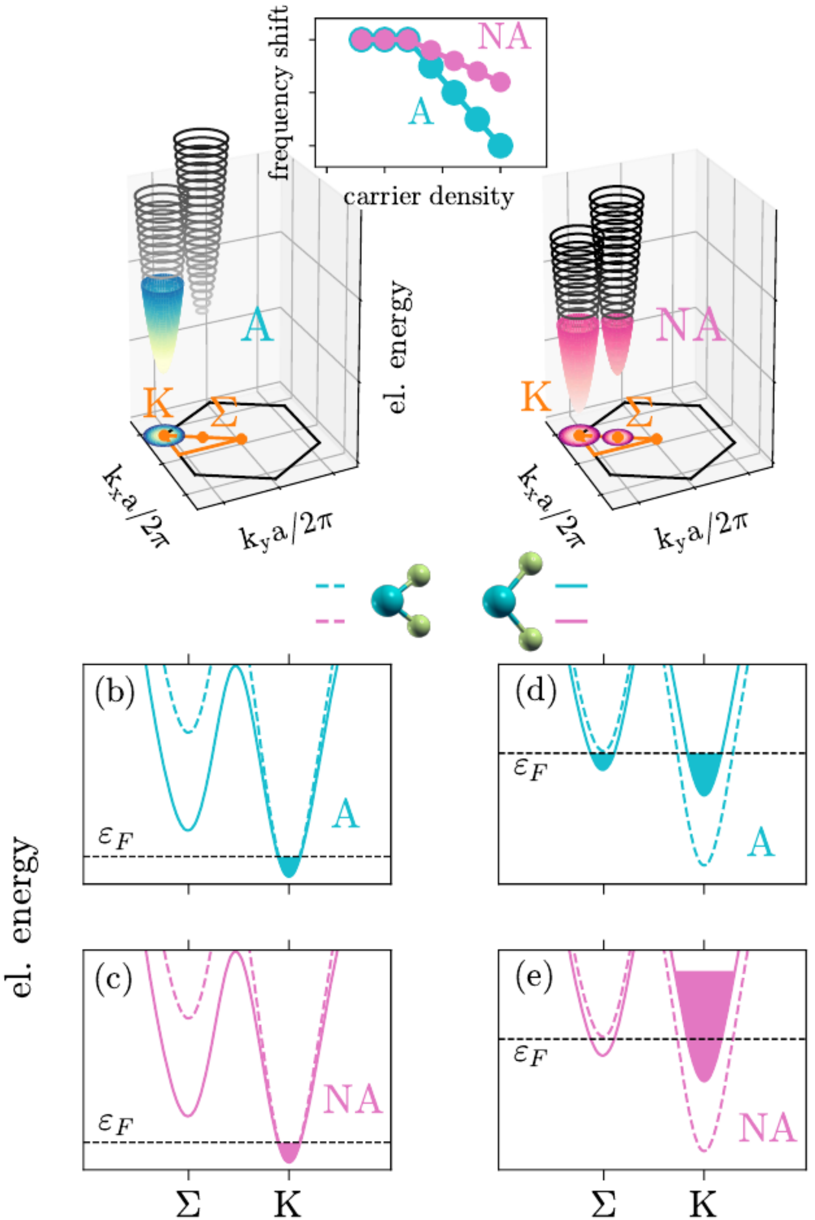
  (i) adiabatic regime – one valley crosses Fermi level

  (ii) nonadiabatic regime – mutiple valleys cross Fermi level

- el. bands under A_{1g} displacement:

  (i) adiabatic regime – both A and NA approximations give same results

  (ii) nonadiabatic regime – significantly different results for A and NA approximations



Conclusions

- Theoretical description of equilibrium and ultrafast time-resolved vibrational spectroscopy (3TM + MBPT)

Part I

- Ultrafast Raman spectroscopy of the hot E_{2g} mode in MgB_2

Part II

- Breakdown of adiabaticity in single-layer doped TMDs

Collaborations:

MgB_2 dynamics

Emmanuele Cappelluti

Fabio Caruso

Claudia Draxl

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THANK YOU FOR YOUR ATTENTION!