

Graphene Light Scattering, Absorption, and Emission

Eric J Heller, Yuan Yang, Lucas Kocia, Wei Chen,[†] Shiang Fang,[†]
Mario Borunda,[§] and Efthimios Kaxiras[†]

**Support: NSF Center for Integrated Quantum Materials
Harvard University**

Major principles:

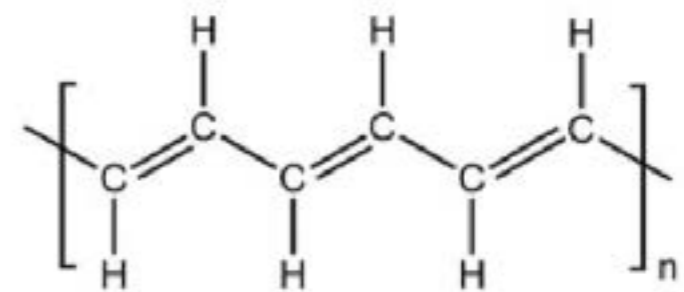
1. We use long established spectroscopic ideas (1926–1932) and especially **free up the electronic transition moments** (i.e. let $\pi \rightarrow \pi^*$ transition moments depend on phonon coordinates, as indeed they must)!
2. **The resulting indirect (phonon assisted) transitions vastly outnumber and often dominate direct (no phonon) transitions,** leading to compelling departures from previous explanations of many experiments

$$\begin{aligned} \mu(\xi) |0\rangle &= \mu(0) |0\rangle + \sum_j \int d\vec{k}_j \left(\frac{\partial \mu(\xi)}{\partial \xi_{k,j}} \right) \xi_{k,j} |0\rangle + \dots = \\ &\mu(0) |0\rangle + \sum_j \int d\vec{k}_j \left(\frac{\partial \mu(\xi)}{\partial \xi_{k,j}} \right) |1_{k,j}\rangle + \dots \end{aligned}$$

We began with polyacetylene... (Incidentally, graphene IS the new polyacetylene!)

1980's: Polyacetylene was the first conducting organic polymer, was expected to revolutionize electronics. Nobel Prizes awarded in 2000 Heeger, MacDiarmid Shirakawa. Its Raman spectrum was not explained until 2015 and that understanding led to insights into graphene.

Raman Scattering in Carbon Nanosystems: Solving Polyacetylene



Research Article

Raman Scattering in Carbon Nanosystems: Solving Polyacetylene

Eric J. Heller ^{†‡}, Yuan Yang [‡], and Lucas Kocia [‡]
[†]Department of Physics and [‡]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

ACS Cent. Sci., 2015, 1 (1), pp 40–49
DOI: 10.1021/acscentsci.5b00021
Publication Date (Web): March 23, 2015
Copyright © 2015 American Chemical Society

Browse the Journal | Articles ASAP | Current Issue | Submission & Review | About the Journal

Mysterious Raman Spectrum Finally Explained

$2\pi/2q$

EJH, Yang, Kocia

Graphene

Strong Fast Pulsed Absorption
and Emission Experiments

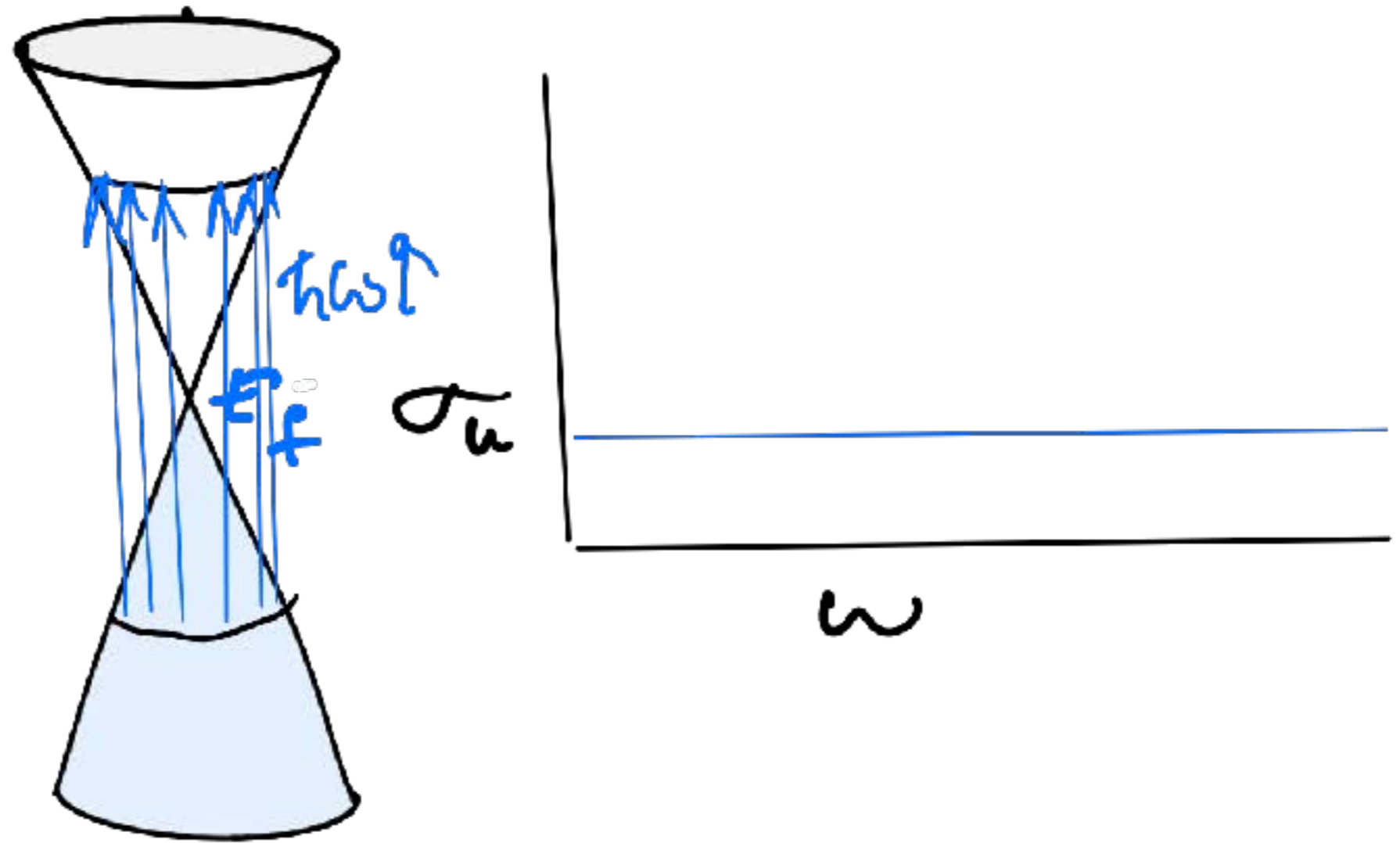
Absorption and Raman Spectroscopy

Strong Fast Pulsed Absorption and Emission

1. VIS-UV absorption spectrum is partially phonon-assisted in nature, especially in the UV, even for weak radiation

I

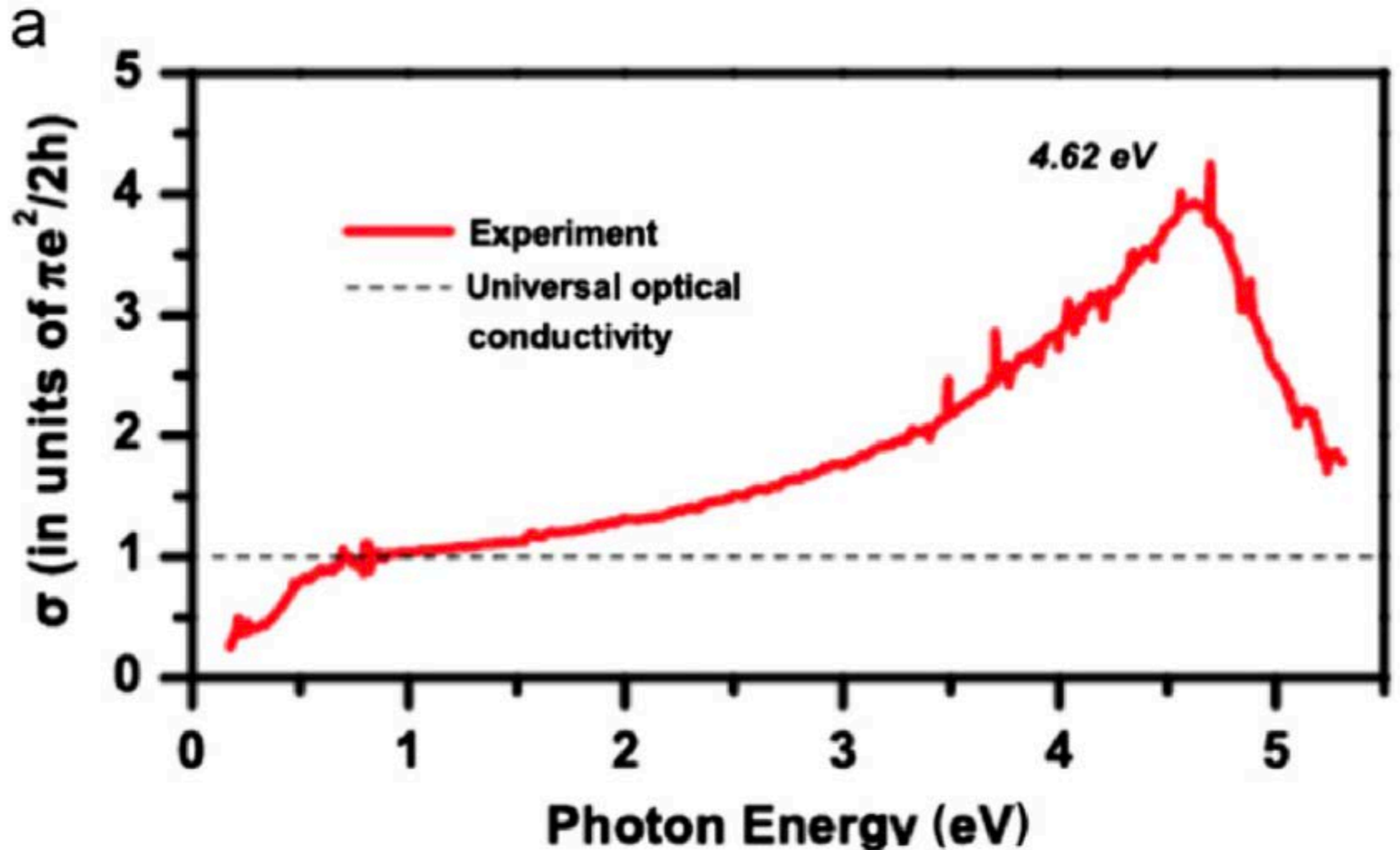
Direct, elastic process counting on linear Dirac cones gives processes growing as ω Division by ω gives the universal constant absorption



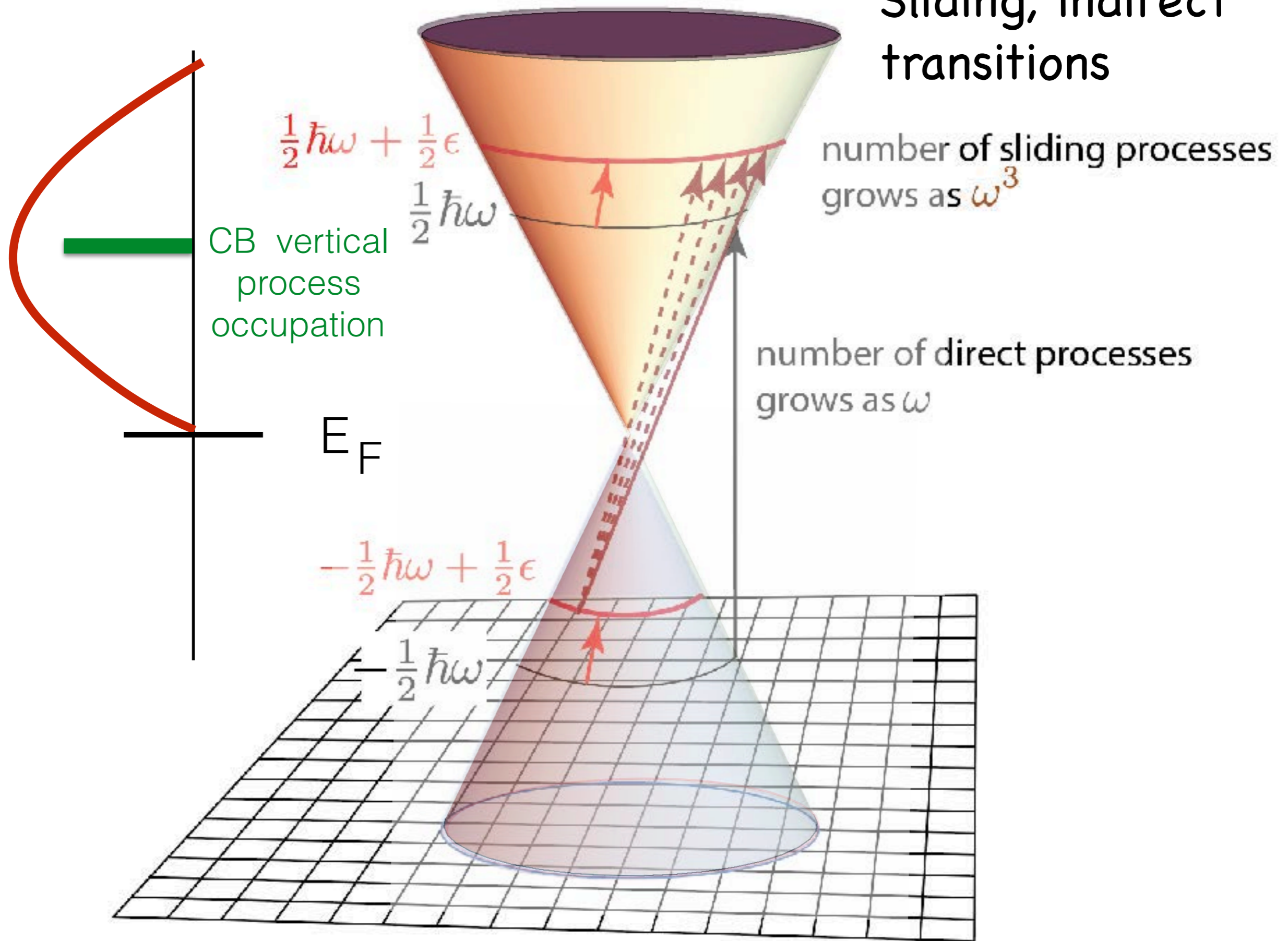
Optical spectroscopy of graphene: From the far infrared to the ultraviolet

Kin Fai Mak^a, Long Ju^b, Feng Wang^{b,c,*}, Tony F. Heinz^{a,**}

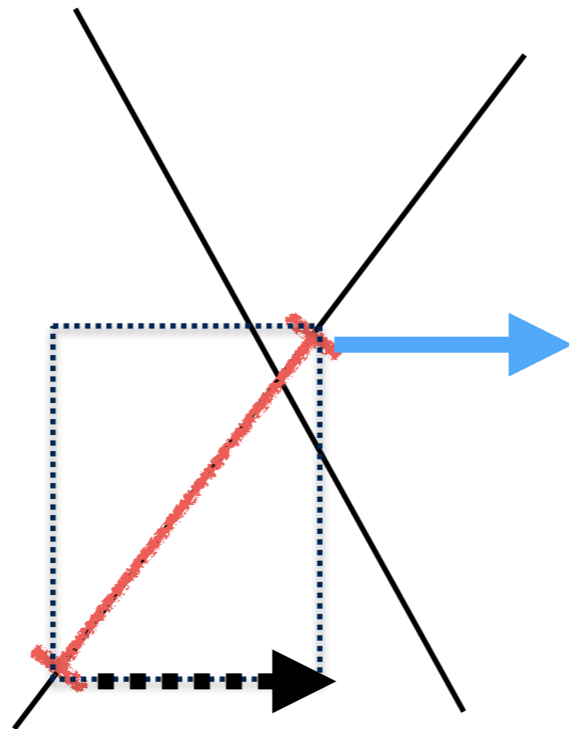
“Universal” more honored in the breach than the observance



Sliding, indirect transitions



Amplitude is coherently summed over all the sliding transitions; same phonon for each

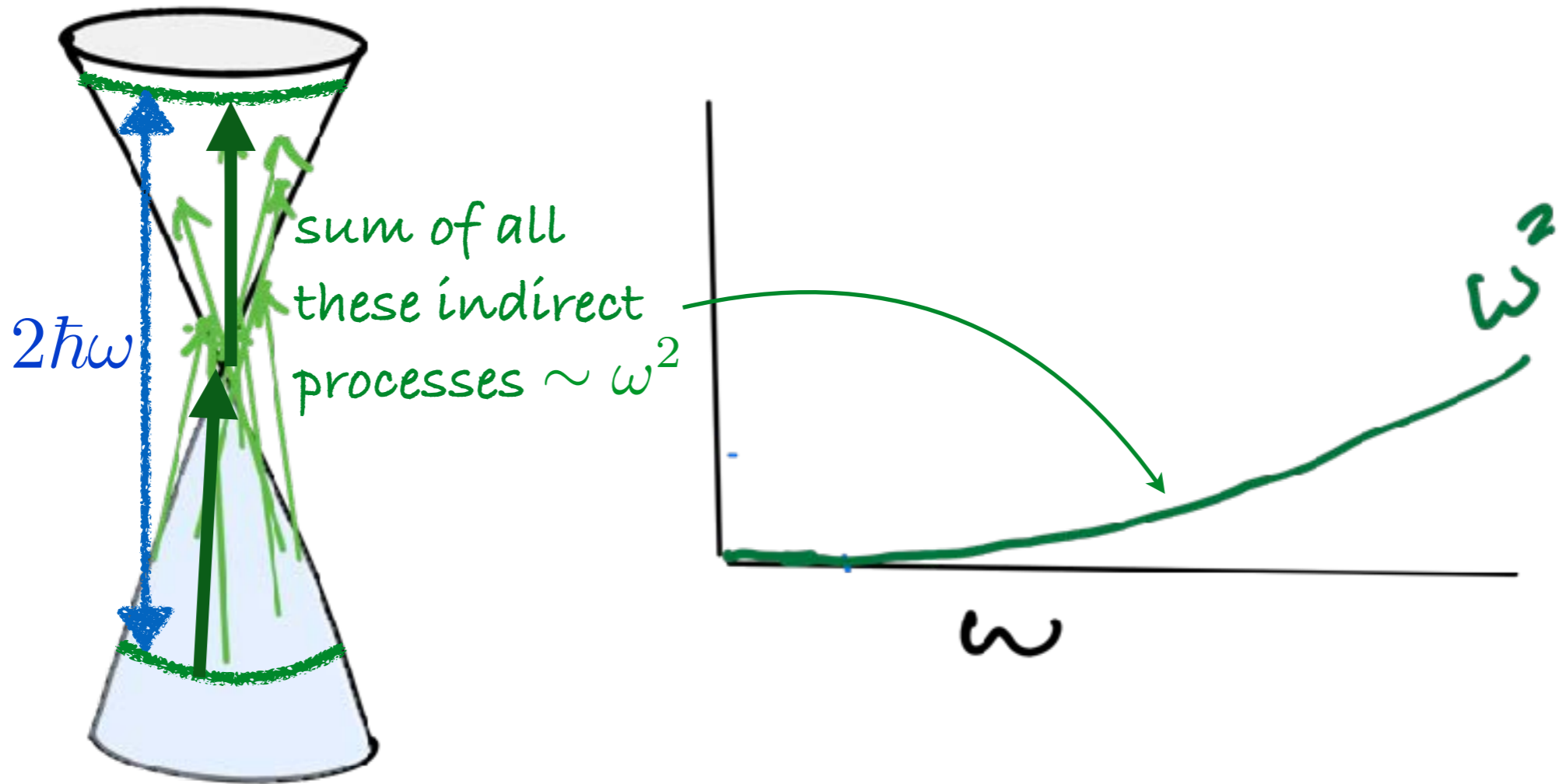


$$\mu(\xi) |0\rangle = \mu(0) |0\rangle + \sum_j \int d\vec{k}_j \left(\frac{\partial \mu(\xi)}{\partial \xi_{k,j}} \right) \xi_{k,j} |0\rangle + \dots =$$

$$\mu(0) |0\rangle + \sum_j \int d\vec{k}_j \left(\frac{\partial \mu(\xi)}{\partial \xi_{k,j}} \right) |1_{k,j}\rangle + \dots$$

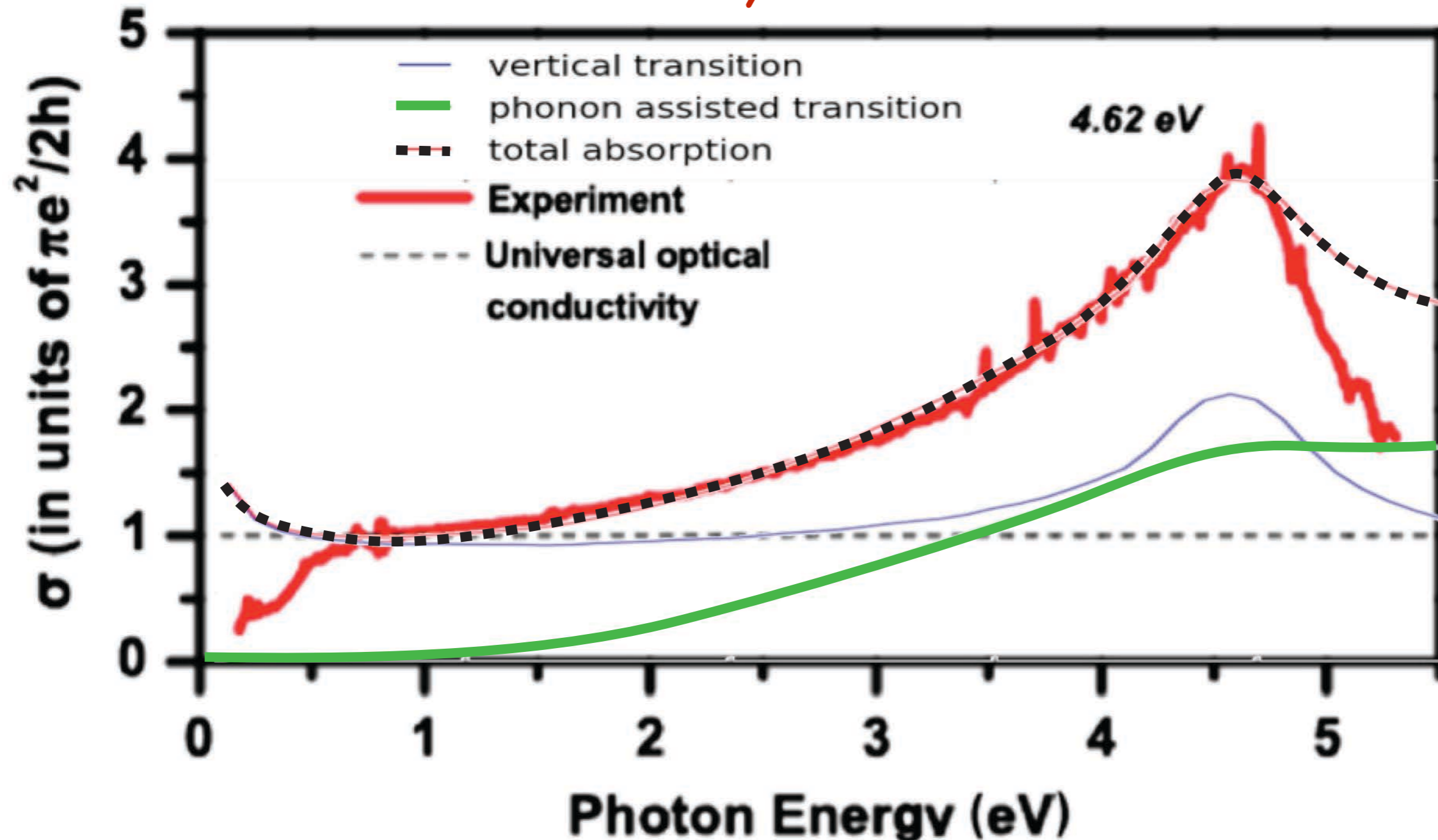
II

The sum of all the inelastic, non-vertical processes of frequency ω for $E_f=0$ goes as ω^2 . All the arrows below have the same vertical rise

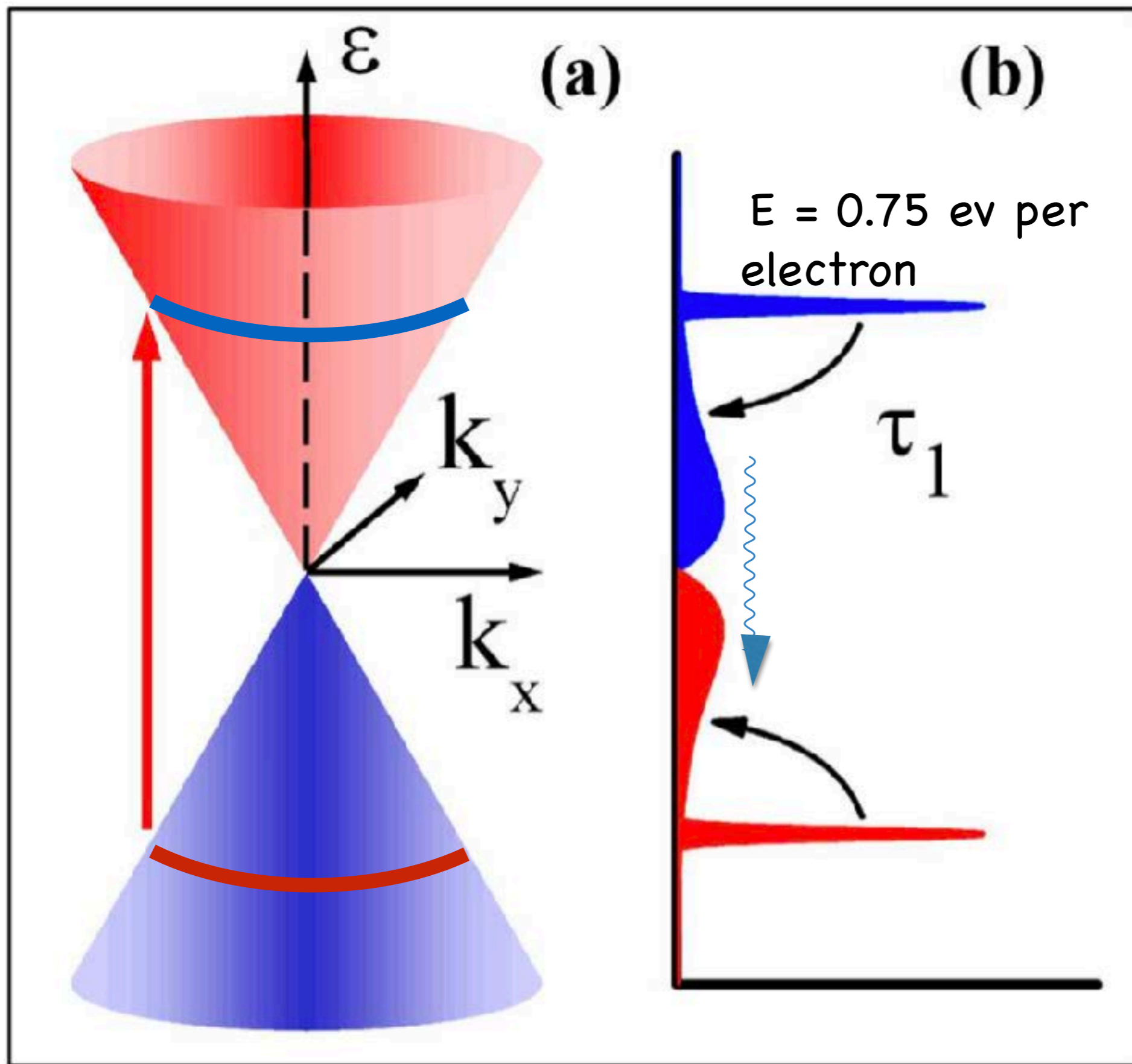


TB-DFT using modified wave functions in presence of phonon distortions to get the T.M.

NO electron-phonon scattering - just Born-Oppenheimer and Franck-Condon theory

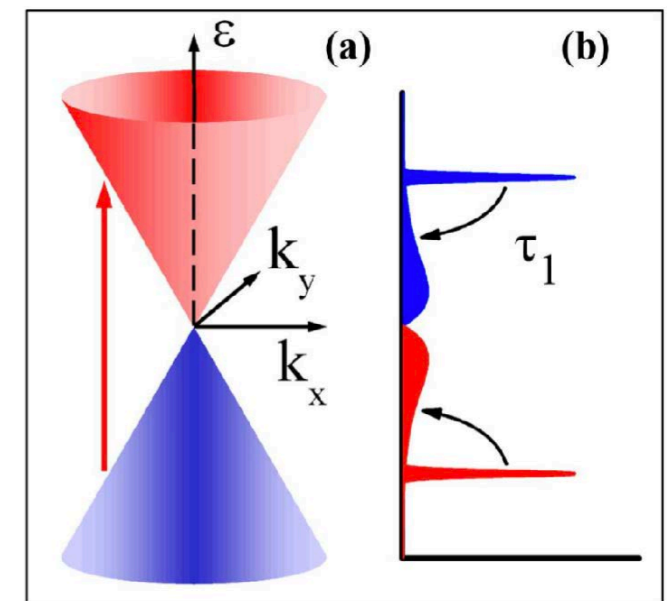
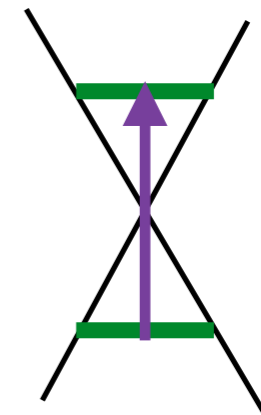
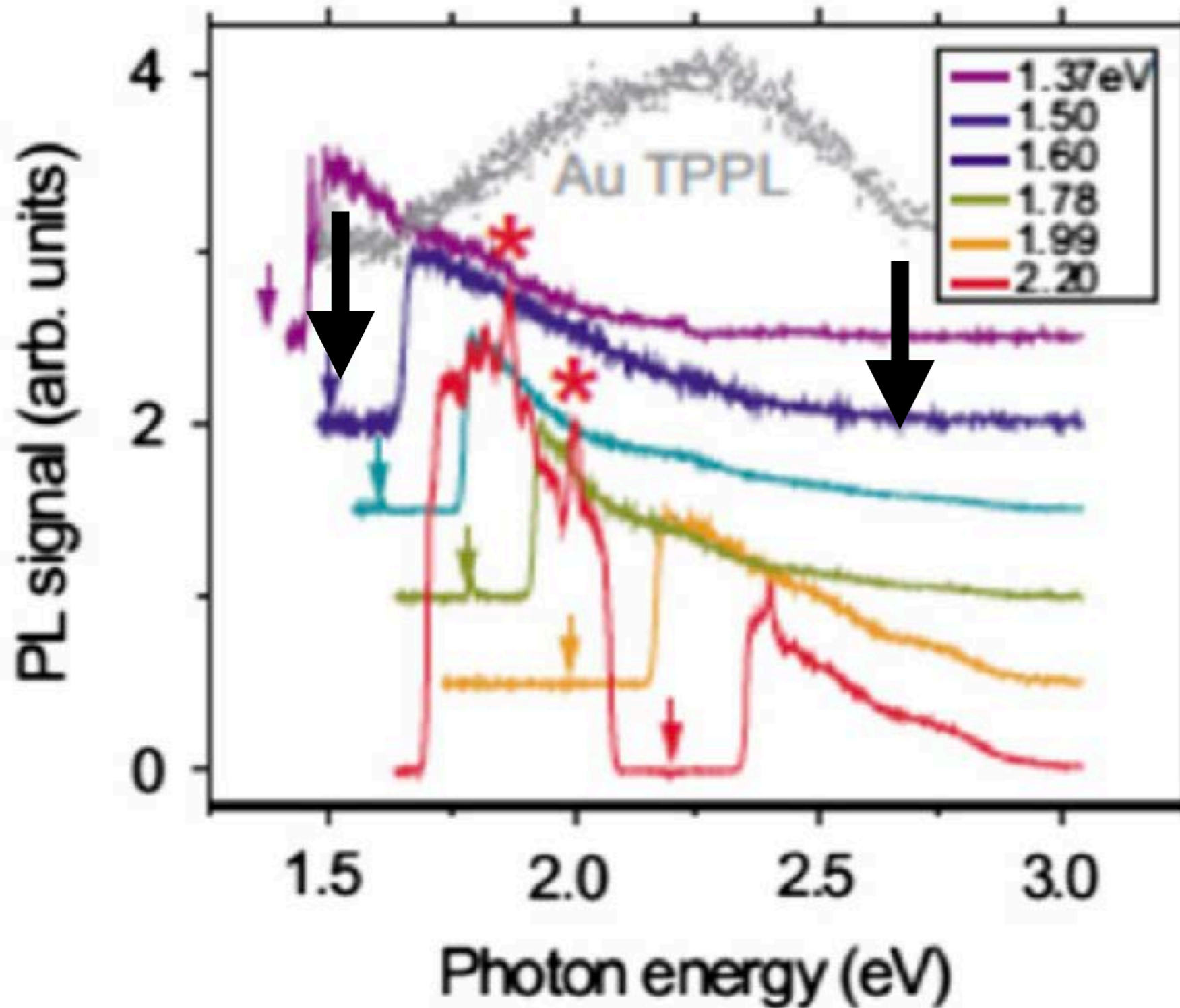


Strong Fast Pulsed
Absorption and Emission



Emission to the blue of 30 fs pulses

Wang-Heinz



Ultrafast luminescence- blackbody emission?

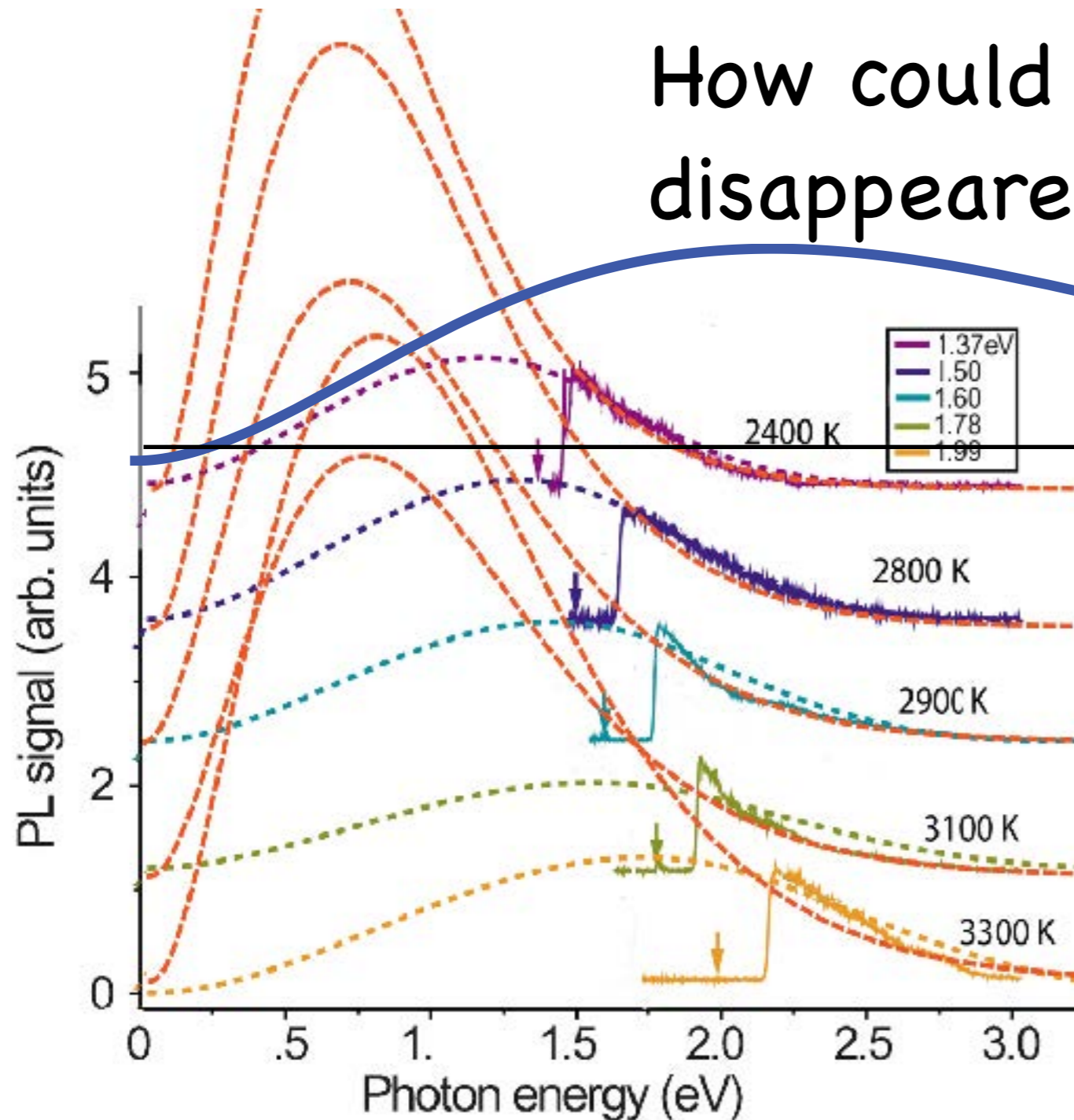
T should have been about 9000K!!

$$kT = 0.75 \text{ V}$$

2/3 of the energy of the electrons have to be removed to get a fit.

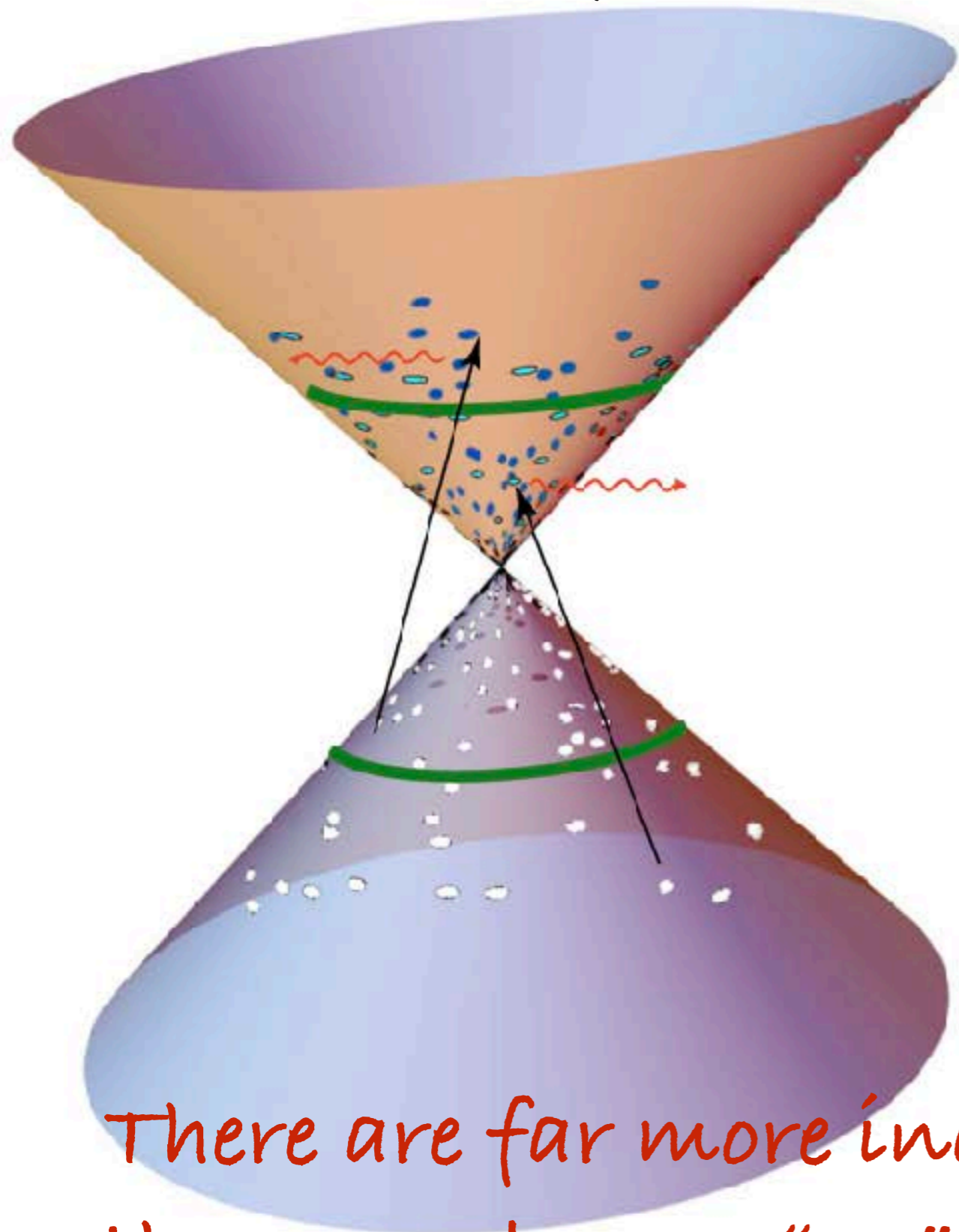
How could the energy have disappeared in under a couple of fs?

9000 K



The observed emission temperatures give us insight into the emission process. If all of the absorbed laser energy were retained in the electronic system, the low electronic specific heat of graphene would lead to an electronic temperature reaching $T_{el} \sim 9000$ K for $F = 0.33$ J m⁻². This is incompatible with the $T_{em} = 3180$ K extracted from experiment. Therefore, a significant fraction of the deposited energy must leave the electronic system during the emission process. Since lateral diffusion of energy can be ruled out from the time scale, we conclude that energy transfer to other degrees of freedom must occur. In the limit of complete equilibration with all phonon degrees of freedom, i.e., considering the full specific heat of graphene [20], we predict a temperature rise of only 380 K. Thus partial equilibration with the phonons must be considered.

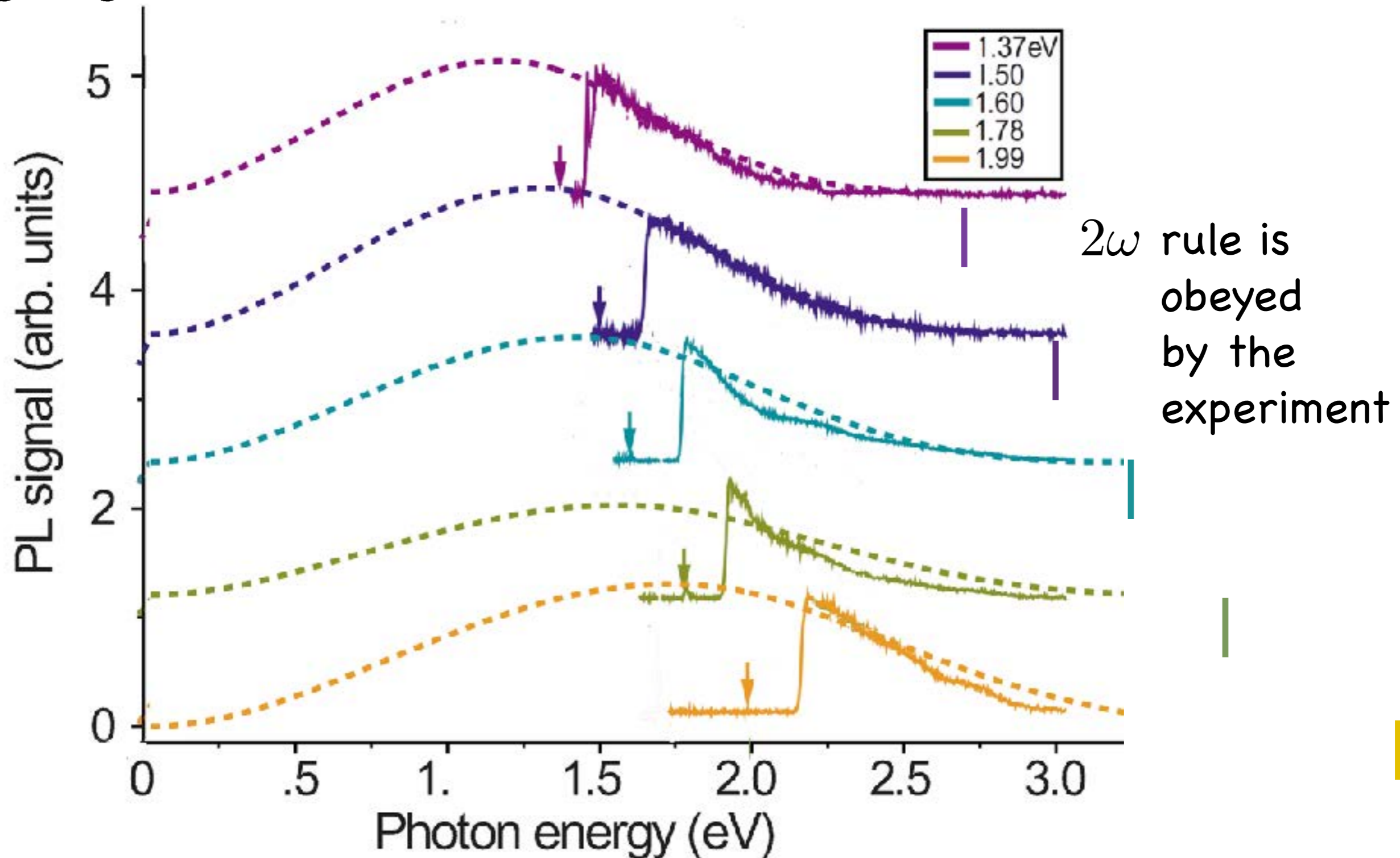
Indirect absorption



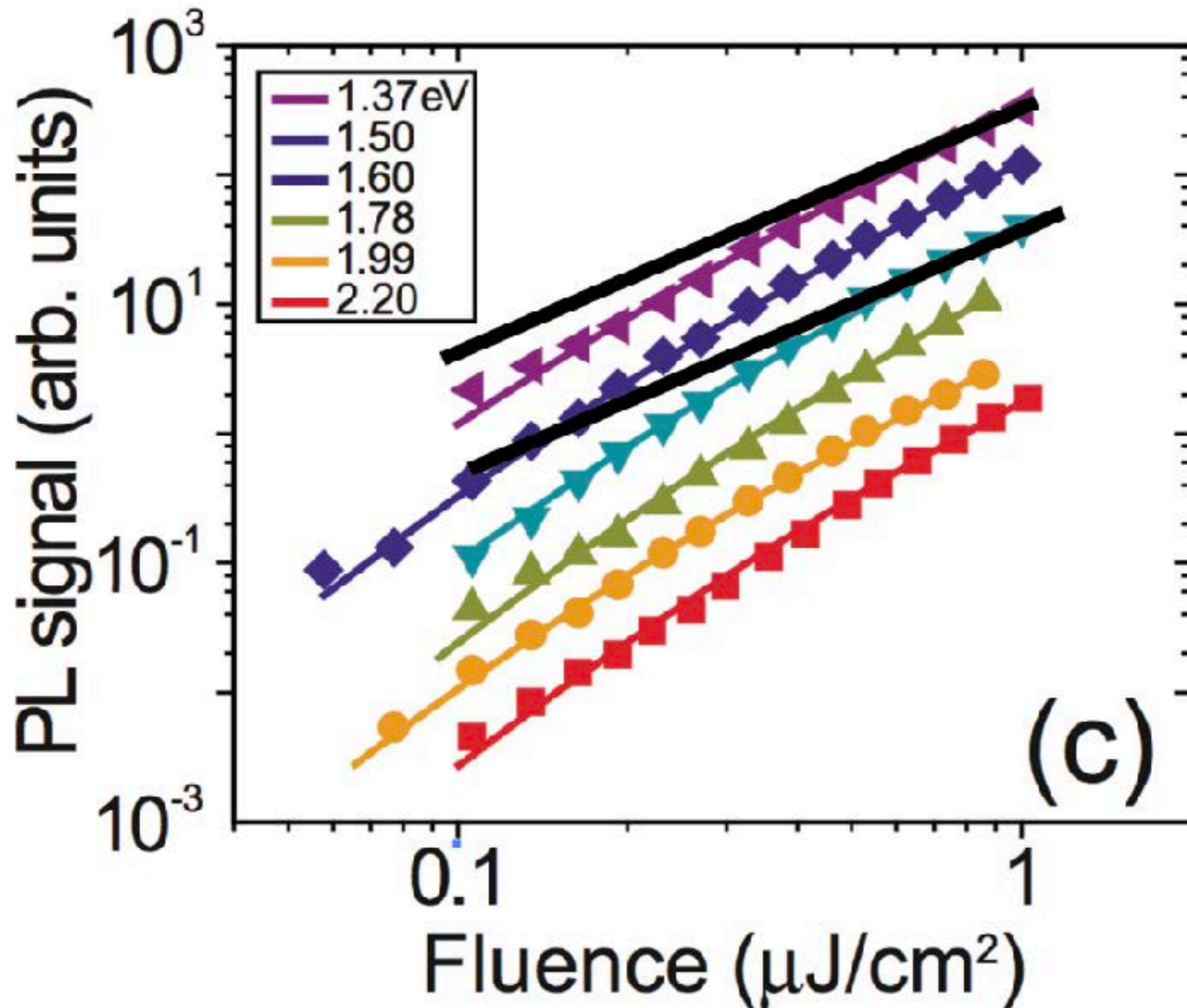
There are far more ind
they are always "on"

Indirect absorption-indirect emission prediction, no adjustable parameters

No relaxation, *no ad-hoc energy removal*. Instant (no lag) agreement.



Indirect mechanism for e-h population and emission predicts fluence² photoluminescence strength



Conclusions:

Ultrafast e-e relaxation is not supported by the data

Phonon assisted transitions are ubiquitous

Graphene

Absorption and Raman Spectroscopy

Extending Kramers–Heisenberg–Dirac Raman theory to 2D crystals 2016

ACS NANO

www.acsnano.org

Theory of Graphene Raman Scattering

Eric J. Heller,^{*,†,‡} Yuan Yang,[‡] Lucas Kocia,[‡] Wei Chen,[†] Shiang Fang,[†] Mario Borunda,[§] and Efthimios Kaxiras[†]

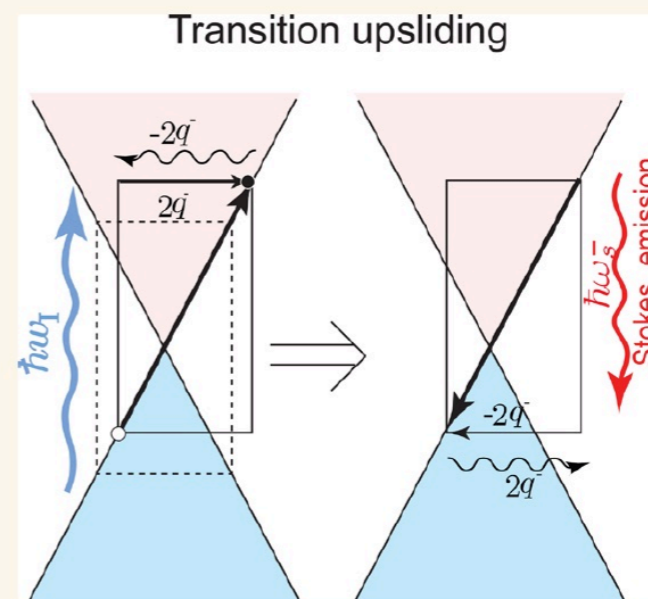
[†]Department of Physics, Harvard University, Cambridge, Massachusetts 02138, United States

[‡]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

[§]Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078, United States

S Supporting Information

ABSTRACT: Raman scattering plays a key role in unraveling the quantum dynamics of graphene, perhaps the most promising material of recent times. It is crucial to correctly interpret the meaning of the spectra. It is therefore very surprising that the widely accepted understanding of Raman scattering, *i.e.*, Kramers–Heisenberg–Dirac theory, has never been applied to graphene. Doing so here, a remarkable mechanism we term “transition sliding” is uncovered, explaining the uncommon brightness of overtones in graphene. Graphene’s dispersive and fixed Raman bands, missing bands, defect density and laser frequency dependence of band intensities, widths of overtone bands, Stokes, anti-Stokes anomalies, and other known properties emerge simply and directly.

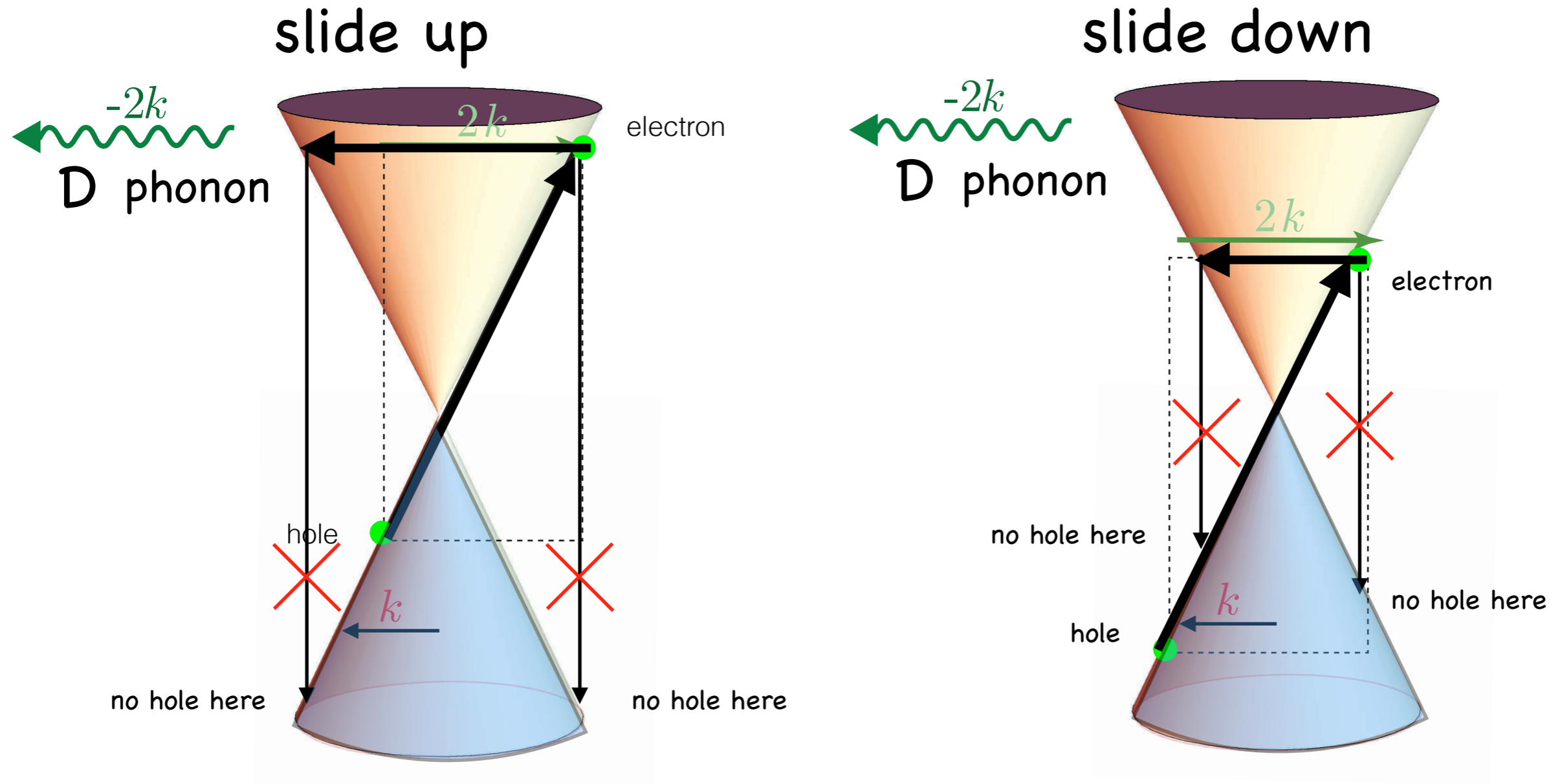


KEYWORDS: Raman spectroscopy, quantum chemistry, resonance theory, theoretical chemistry, UV–vis spectroscopy

KHD is circa 1926 2nd order light-matter perturbation theory, with transition moments that may depend on phonon coordinates. It has been used for 90 years, even to explain PAH's

"double resonance," circa 2000 and used only in the carbon community, is a different theory, 4th order perturbation theory with fixed transition moments.

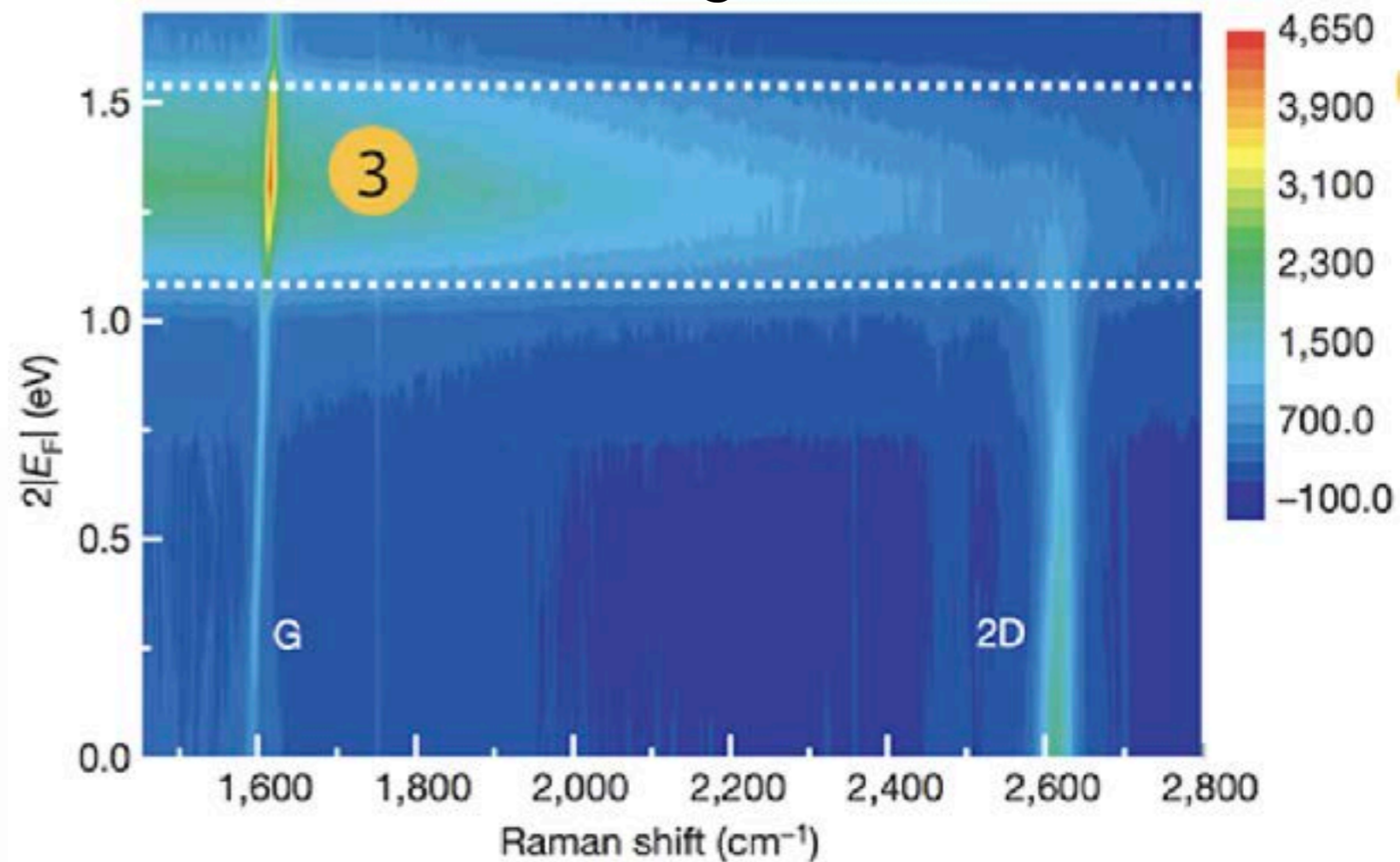
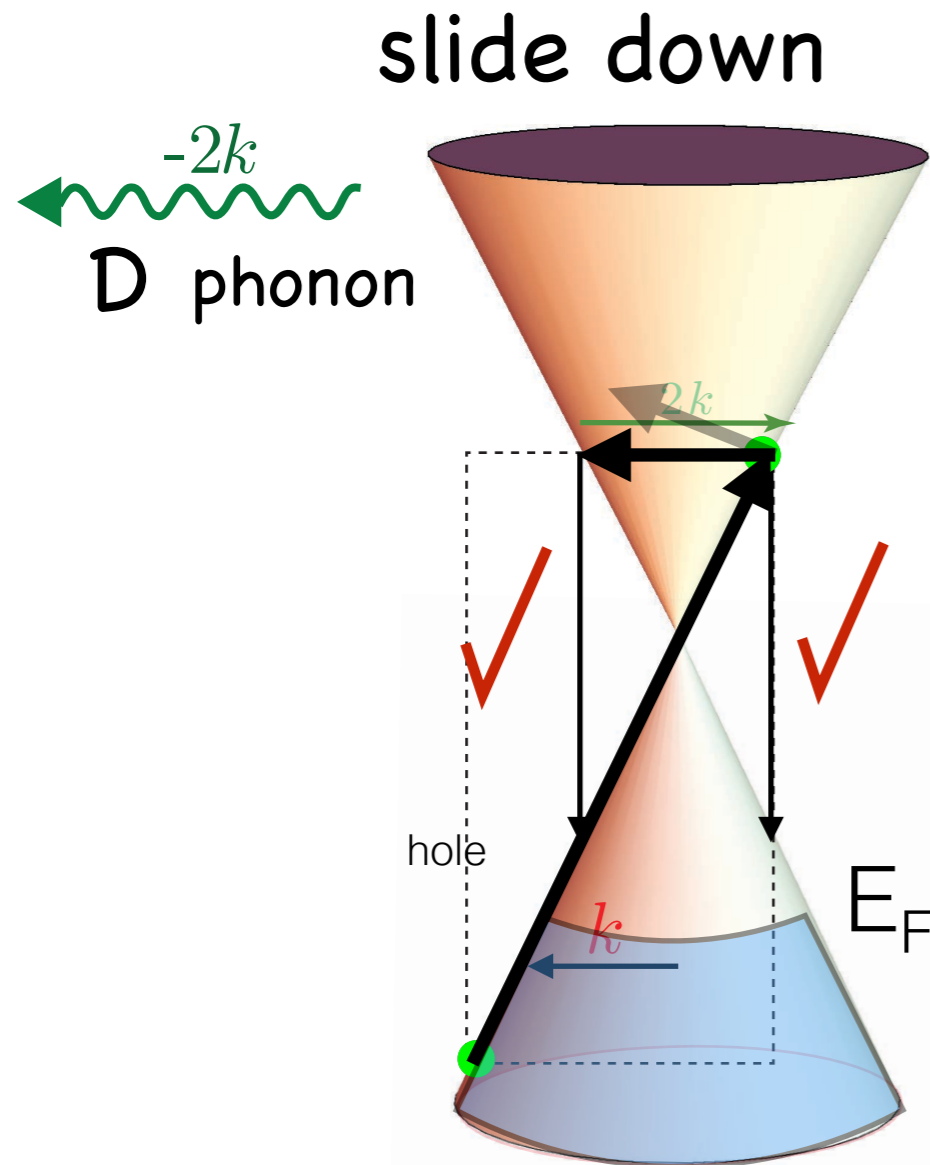
Sliding transitions are Pauli blocked in emission



This sliding transition cannot emit a Raman photon—Pauli blocked

Many sliding D transitions become allowed with **hole doping** - leading to bright continuum electronic Raman emission

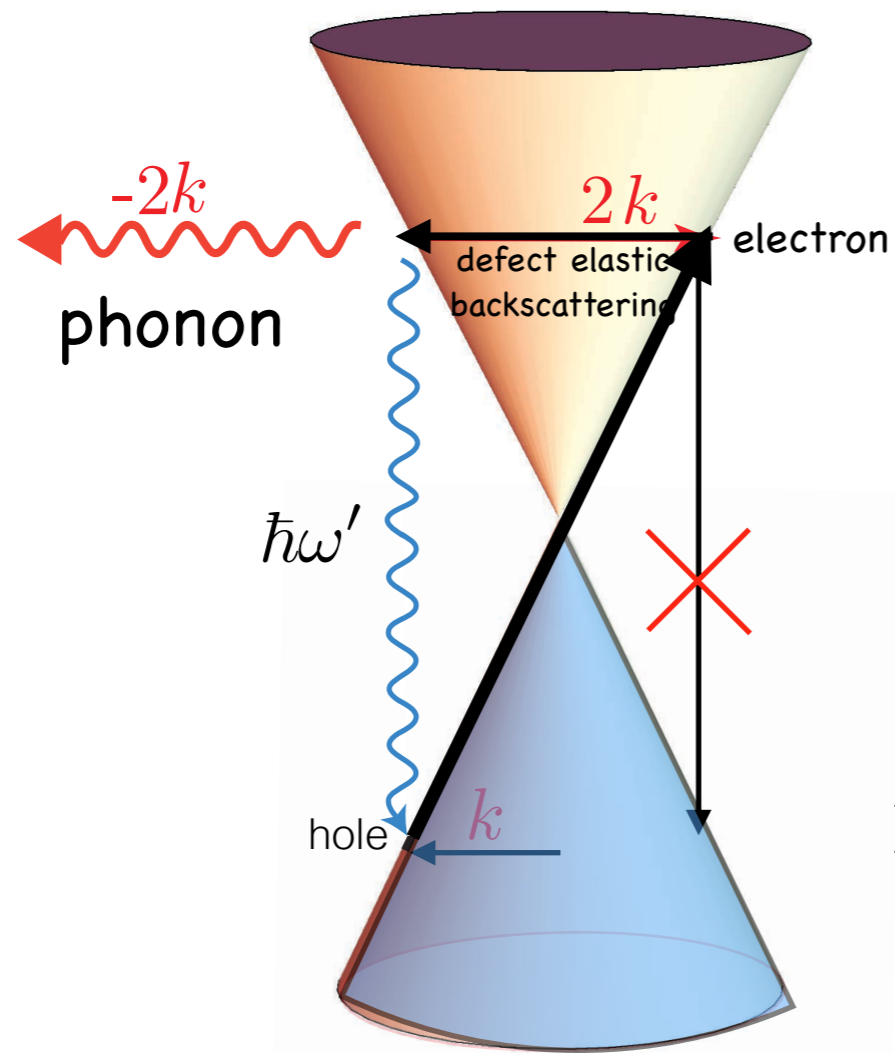
Continuum electronic Raman
100 times brighter than G



(17) Chen, C.-F.; Park, C.-H.; Boudouris, B. W.; Horng, J.; Geng, B.; Girit, C.; Zettl, A.; Crommie, M. F.; Segalman, R. A.; Louie, S. G.; et al. Controlling inelastic light scattering quantum pathways in graphene. *Nature* 2011, 471, 617–620.

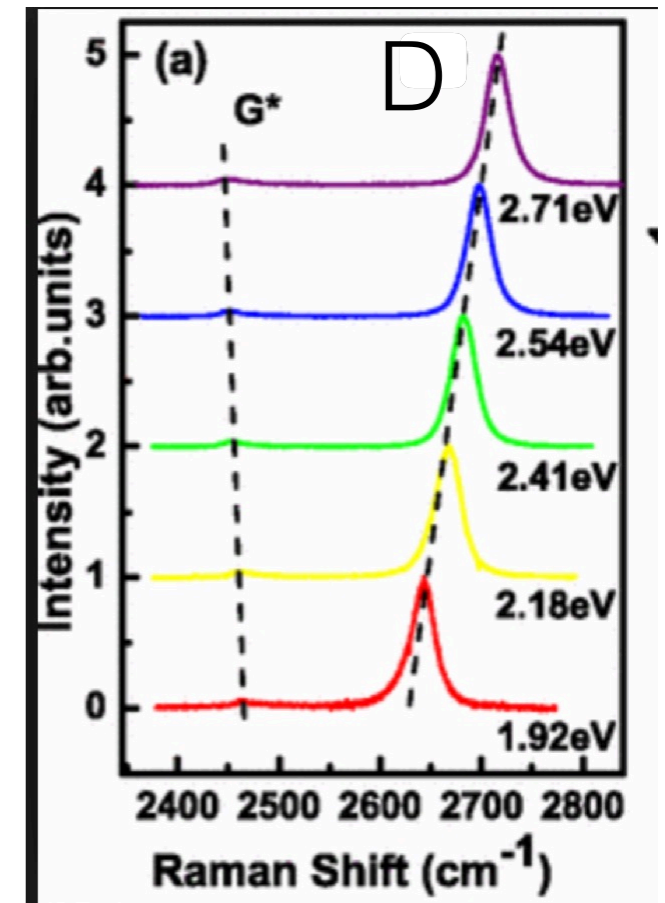
Production of a D phonon requiring defect backscattering to emit

This happens instantly!
No waiting - caused by transition moment



$$E = \hbar\omega_I$$

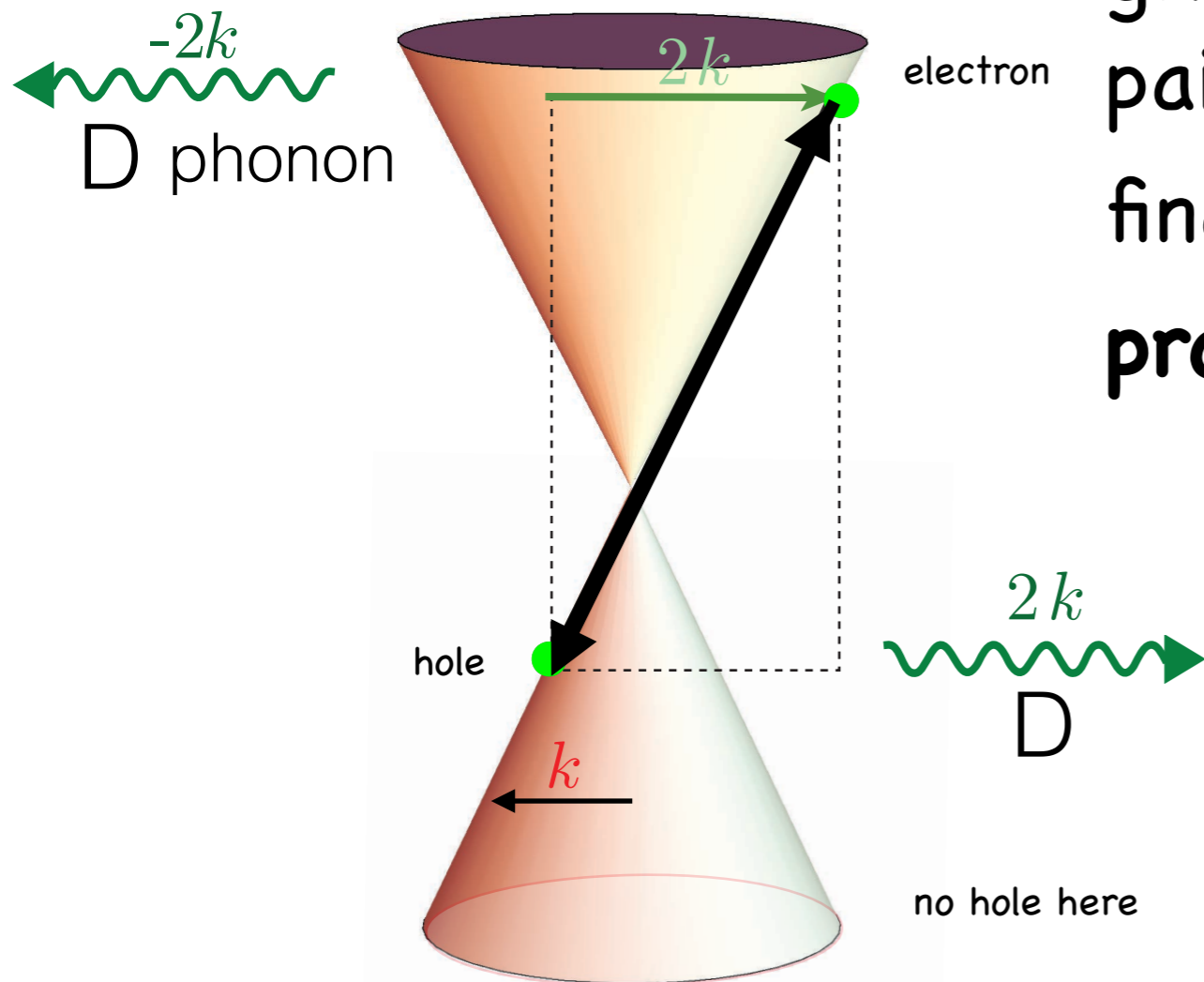
$$\hbar\omega'_i$$



D phonon energy is dispersive with k . About 50 cm^{-1} per eV of electronic energy

Sliding path reversal gives coherent 2D Raman phonons

All linear sliding reversals in a set give identical oppositely heading pairs of phonons, and the same final state of the system, so these processes interfere constructively



$$\sum_{i \rightarrow f}^{\rho, \sigma} = \frac{8\pi e^4 \omega_s^3 \omega_I}{9c^4} |\alpha_{i,f}^{\rho, \sigma}|^2$$

$$\alpha_{m_i m_f}^{\rho, \sigma} = \frac{1}{\hbar} \sum_{v, c, m} \left[\frac{\langle \chi_{m_f}(\xi) | \mu_{q_v, q_c}^{\sigma}(\xi)^{\dagger} | \chi_m(\xi) \rangle \langle \chi_m(\xi) | \mu_{q_c', q_v}^{\rho}(\xi) | \chi_{m_i}(\xi) \rangle}{E_{m_i} - E_{v, c, m} + \hbar\omega_I - i\Gamma_{j, m}} \right]$$

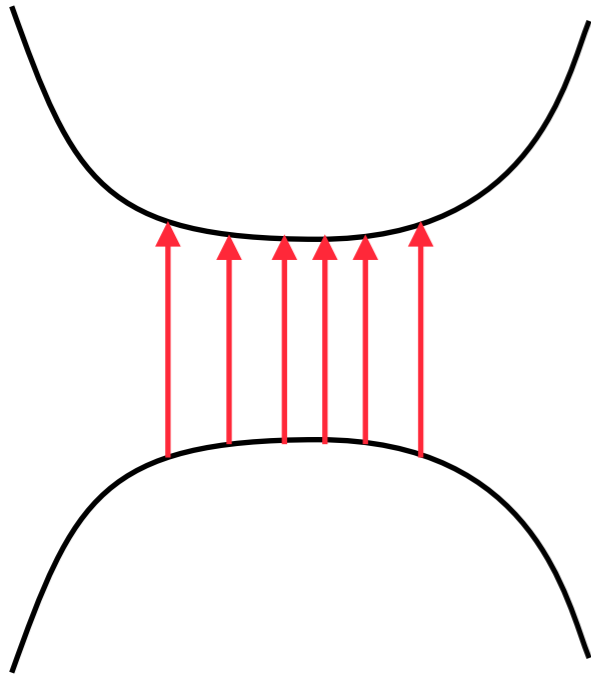
The wellspring of the ultra bright 2D overtone!

$\text{ex}[\mathbf{x}_-, \mathbf{y}_-] :=$

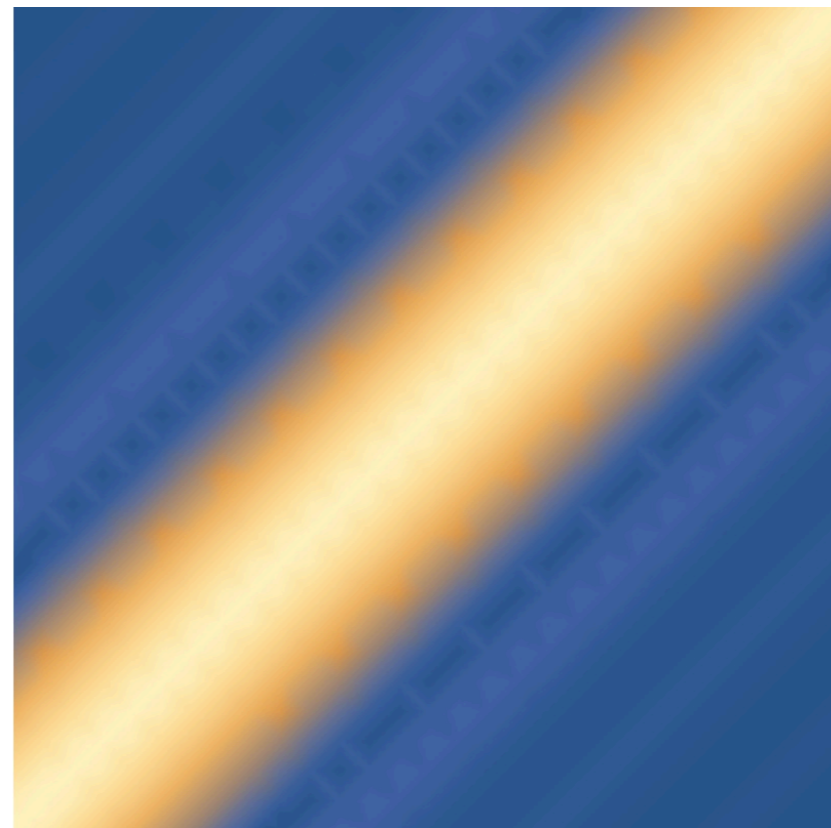
$\text{Integrate}[(\mathbf{a} - \mathbf{s})(\mathbf{a} + \mathbf{s}) \text{Exp}[\mathbf{I} \mathbf{k} (\mathbf{a} - \mathbf{s}) \mathbf{x} + \mathbf{I} \mathbf{k} (\mathbf{a} + \mathbf{s}) \mathbf{y}];$
 $\{\mathbf{s}, -\mathbf{a}, \mathbf{a}\}]$

$$\frac{-2 e^{2 i a k x} (i + a k (x - y)) + 2 e^{2 i a k y} (i + a k (-x + y))}{k^3 (x - y)^3}$$

electron $x \rightarrow$

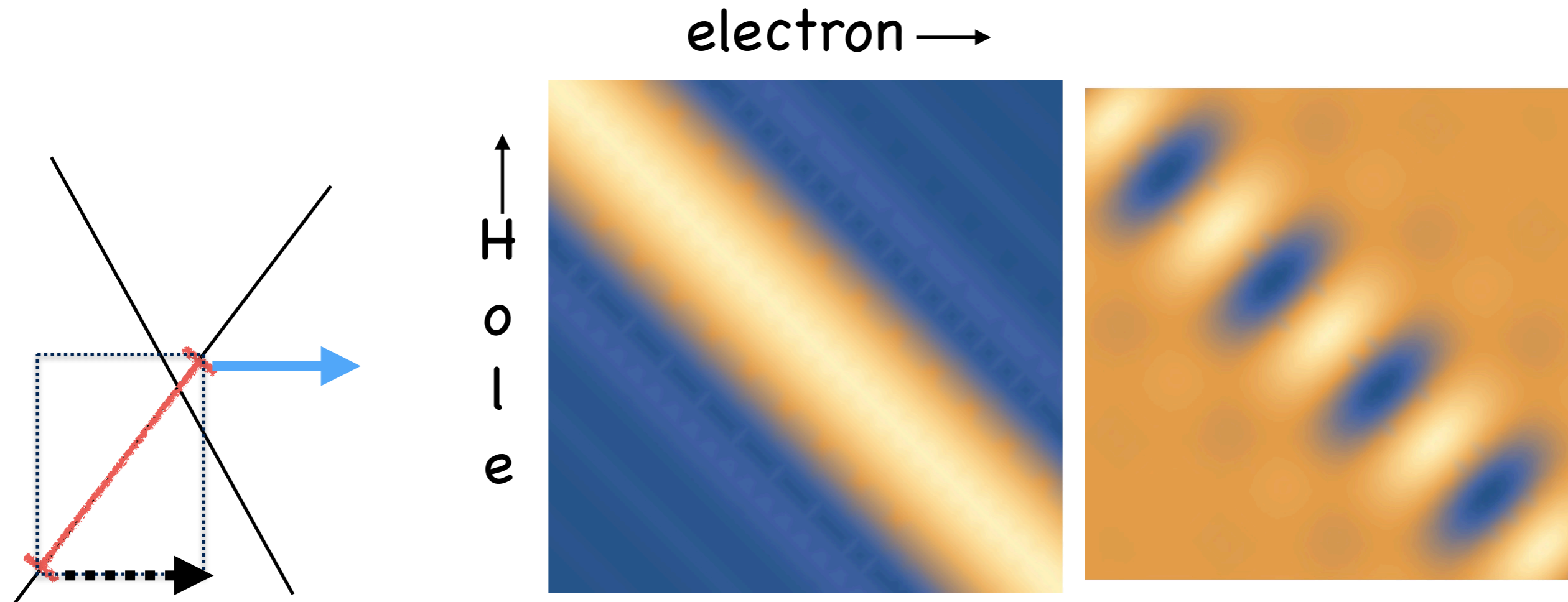


hole $y \uparrow$



Exciton. (Where you find the electron, you find the hole nearby, and vice-versa)

Anti-exciton with momentum



Amplitude is coherently summed over all the sliding transitions; same phonon for each

Doped IR and Far IR light
absorption and sum rule

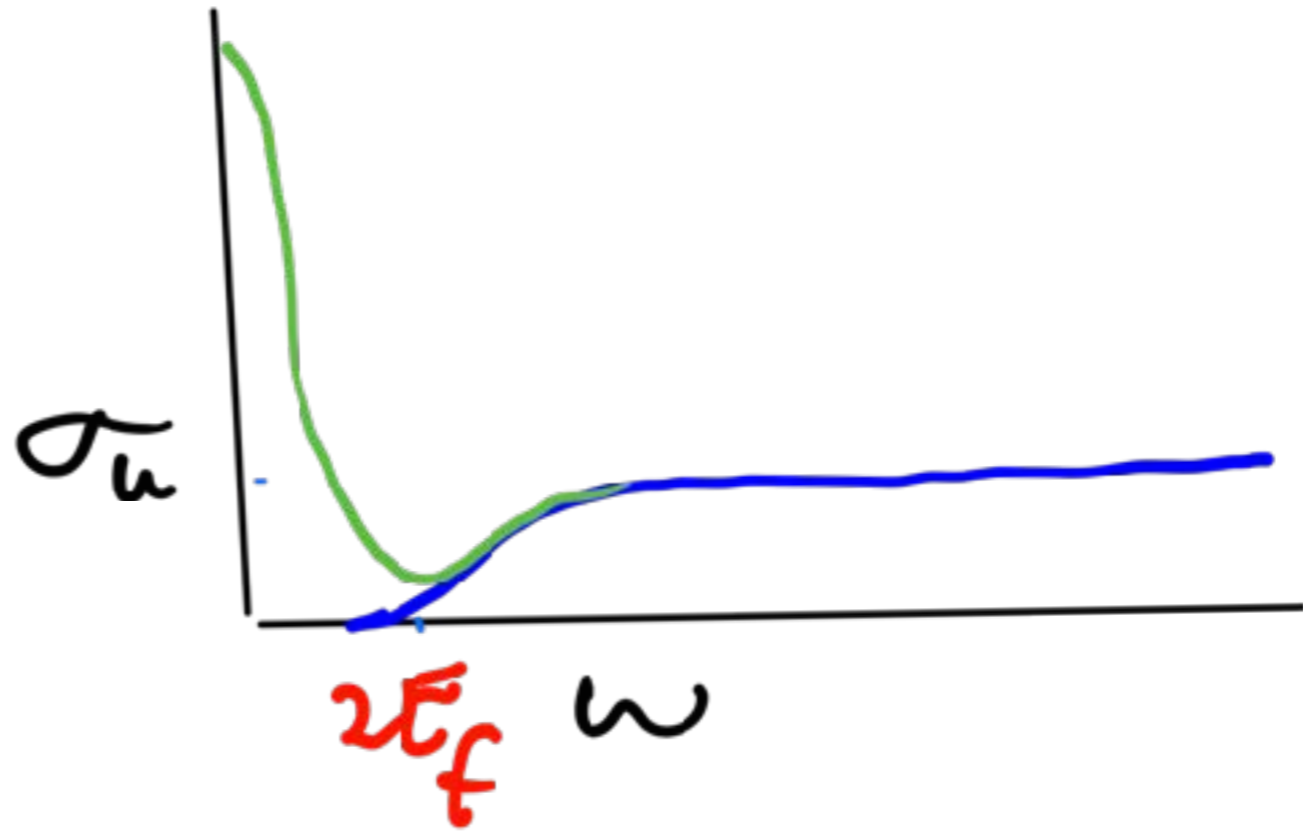
Summary

Weak “universal” absorption, strong pulsed absorption, fast emission, and all major Raman phenomenology fits in one framework, by **unfreezing the electronic transition moments** to allow dependence on phonon displacement, and following the implications.

Phonons abound! Mostly ones you never see....

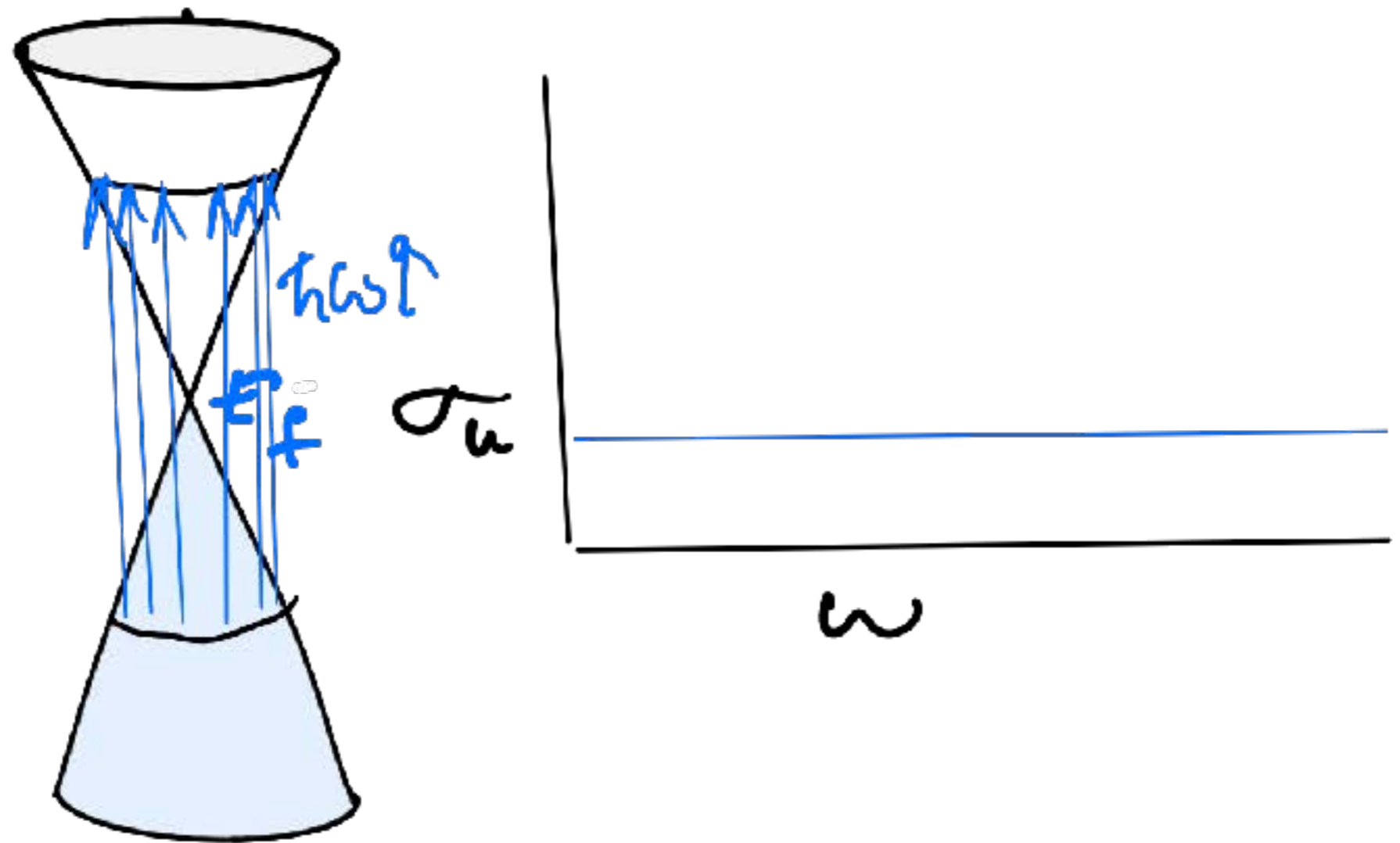
IV

ultimately the vertical processes are a little wobbly since coherence lengths and lifetimes are finite. No phonons are implied, only slightly nonvertical processes are allowed



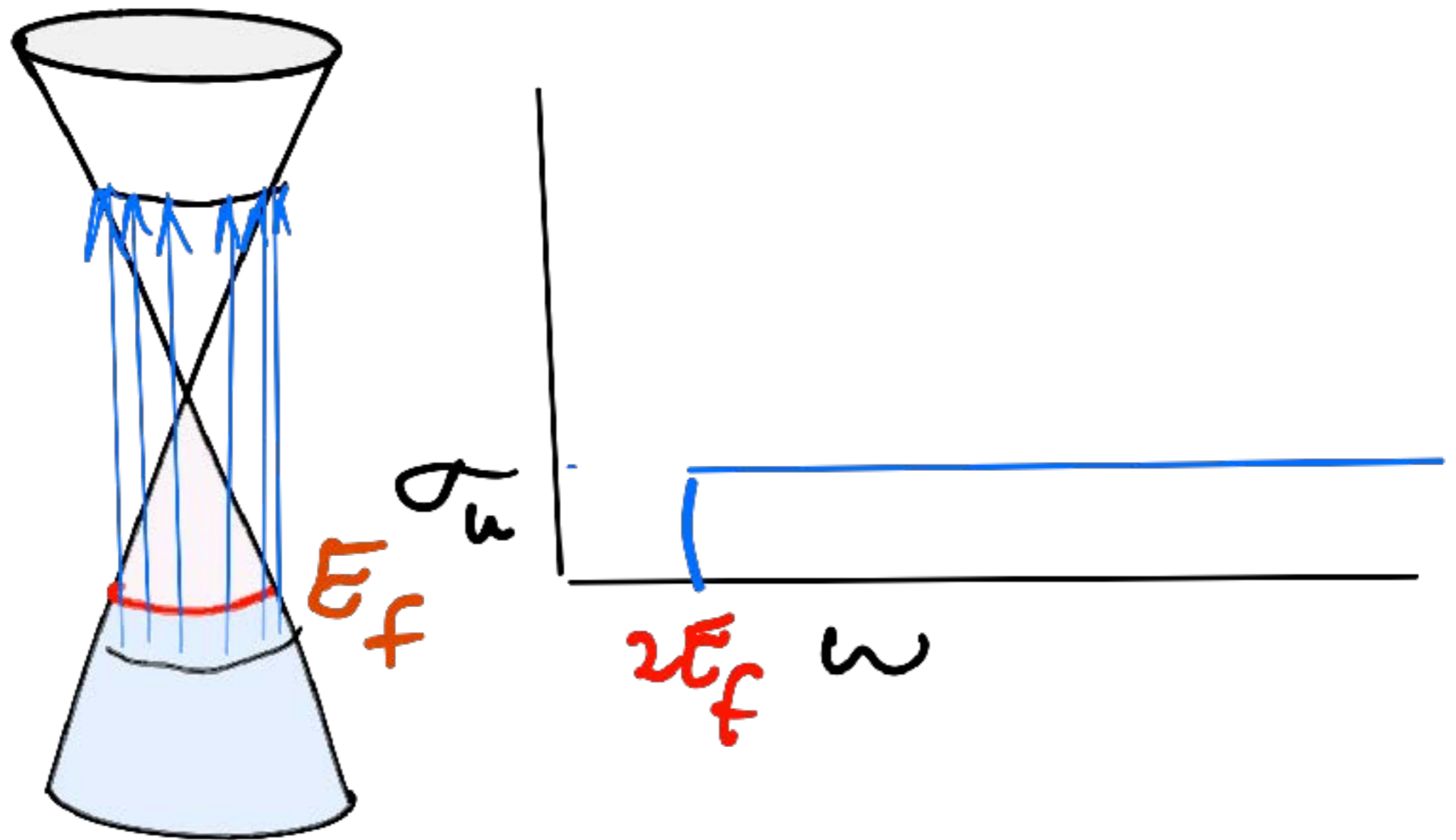
I

Direct, elastic process counting on linear Dirac cones gives processes growing as ω . Division by ω gives the universal constant absorption



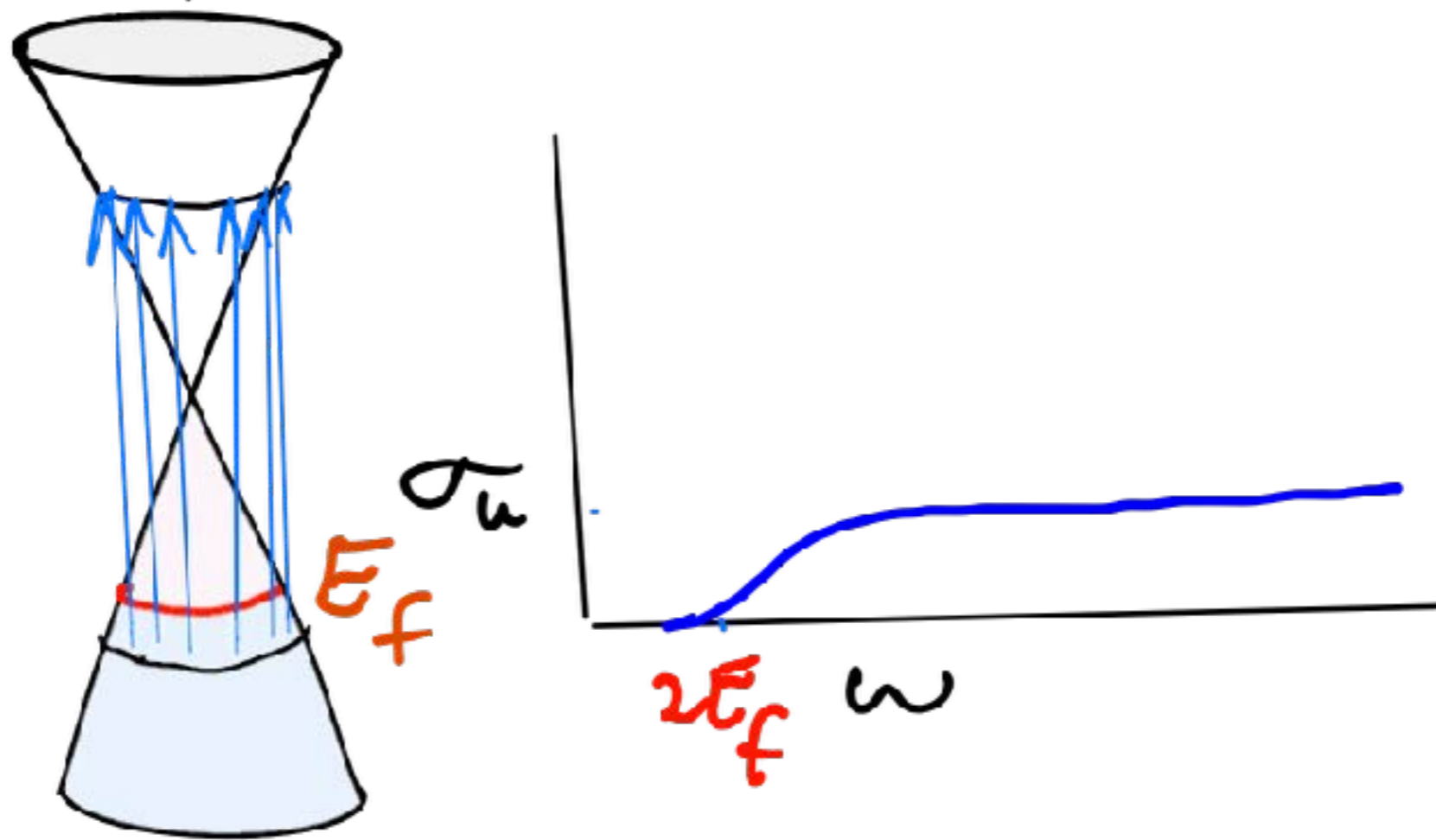
II

uniform doping causes an abrupt termination of the direct process,

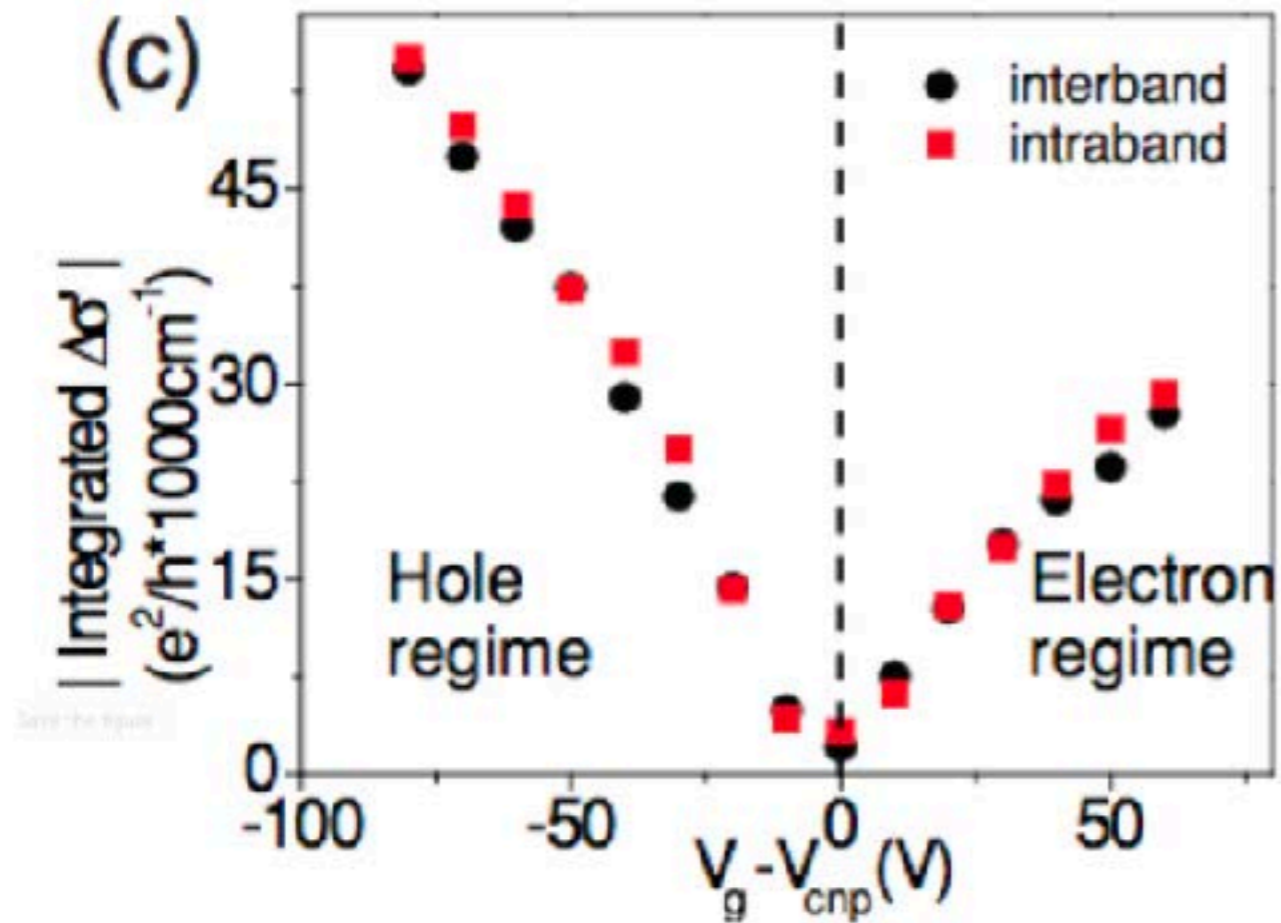


III

Non uniform doping and finite temperature effects cause a softening of the termination



Sum rule for inter and intraband



The beautiful experimental sum rule verified at different dopings has been explained in a puzzling way

Figure 6: Far infrared and infrared region absorption with different biases

Optical spectroscopy of graphene: From the far infrared to the ultraviolet

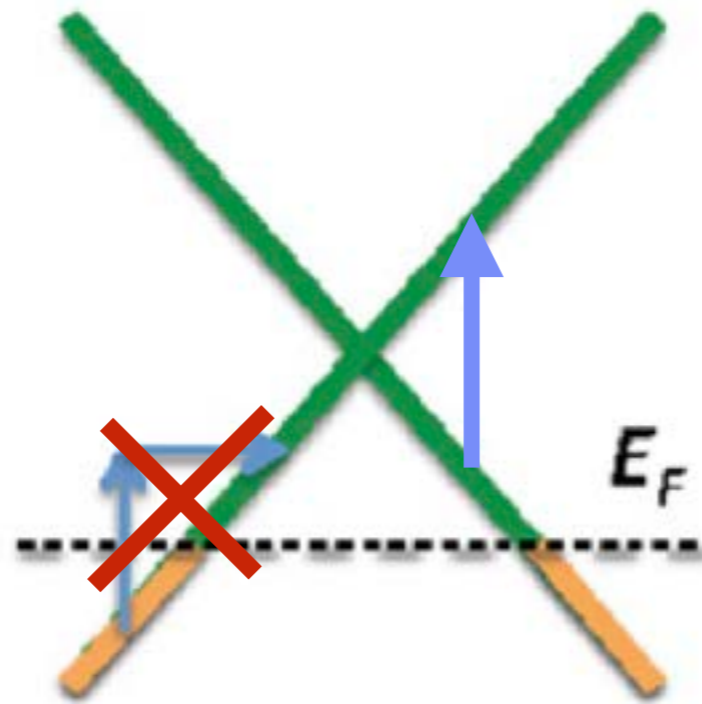
Kin Fai Mak^a, Long Ju^b, Feng Wang^{b,c,*}, Tony F. Heinz^{a,*}

^a Departments of Physics and Electrical Engineering, Columbia University, New York, NY 10027, USA

^b Department of Physics, University of California at Berkeley, Berkeley, CA 94720, USA

^c Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Indirect processes are used to justify far infrared excess

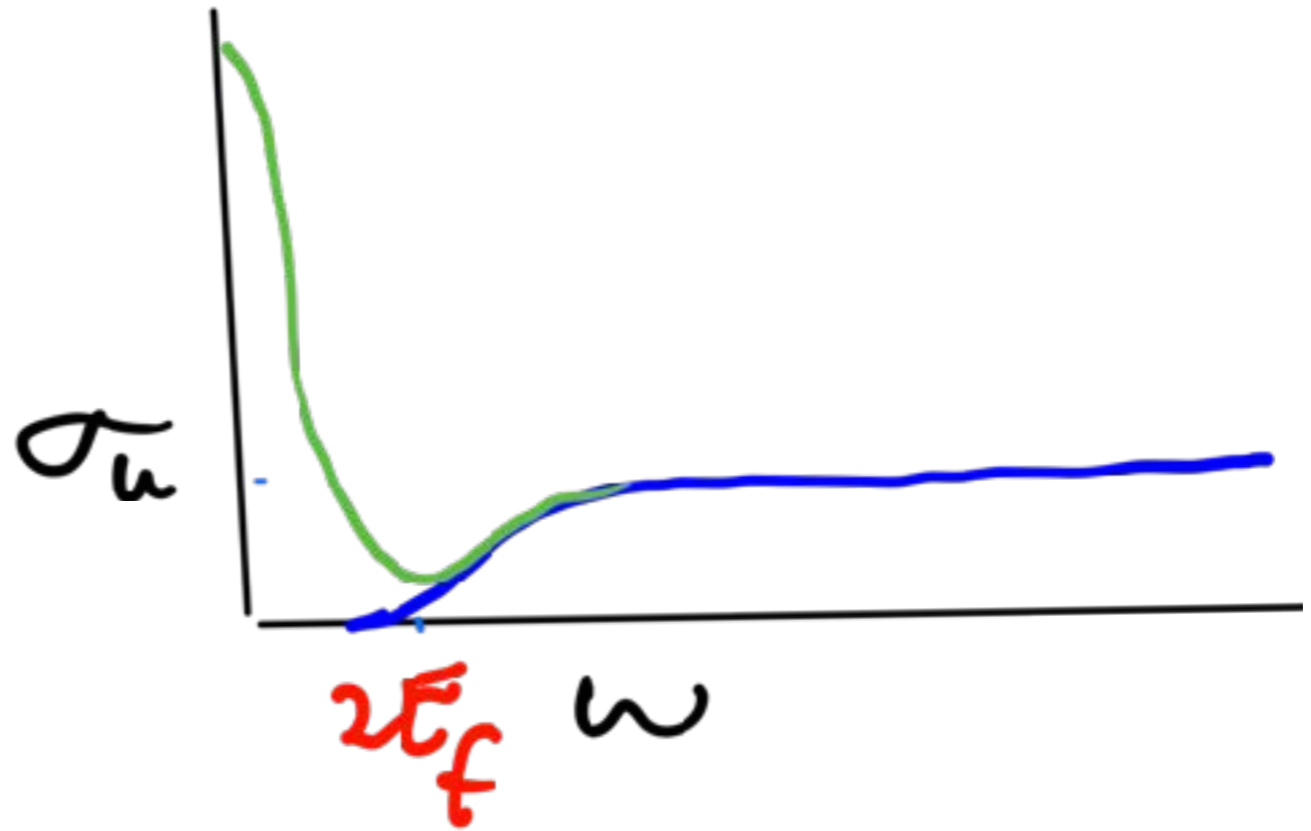
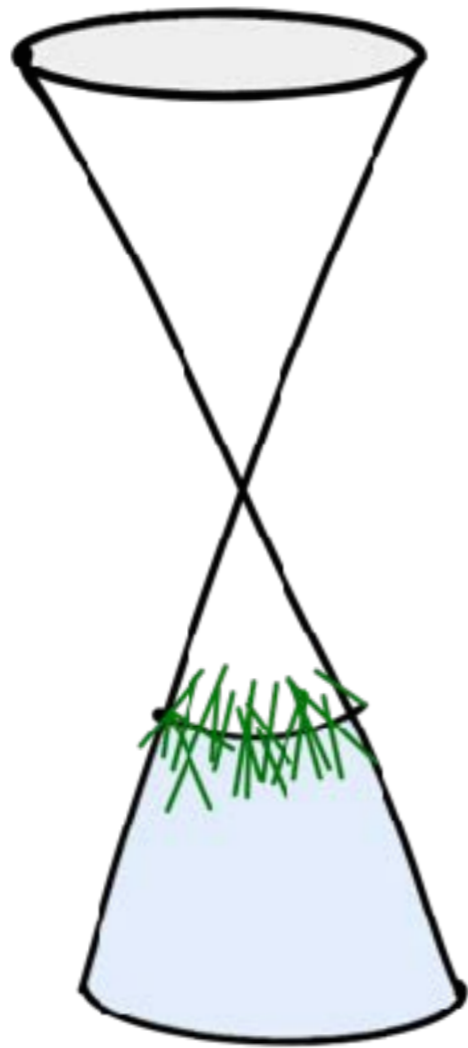


Missing direct processes explain infrared deficit

Trouble: these two distinct types of processes differ by a phonon production matrix element, spoiling the sum rule.

IV

ultimately the vertical processes are a little wobbly since coherence lengths and lifetimes are finite. No phonons are implied, only slightly nonvertical processes are allowed



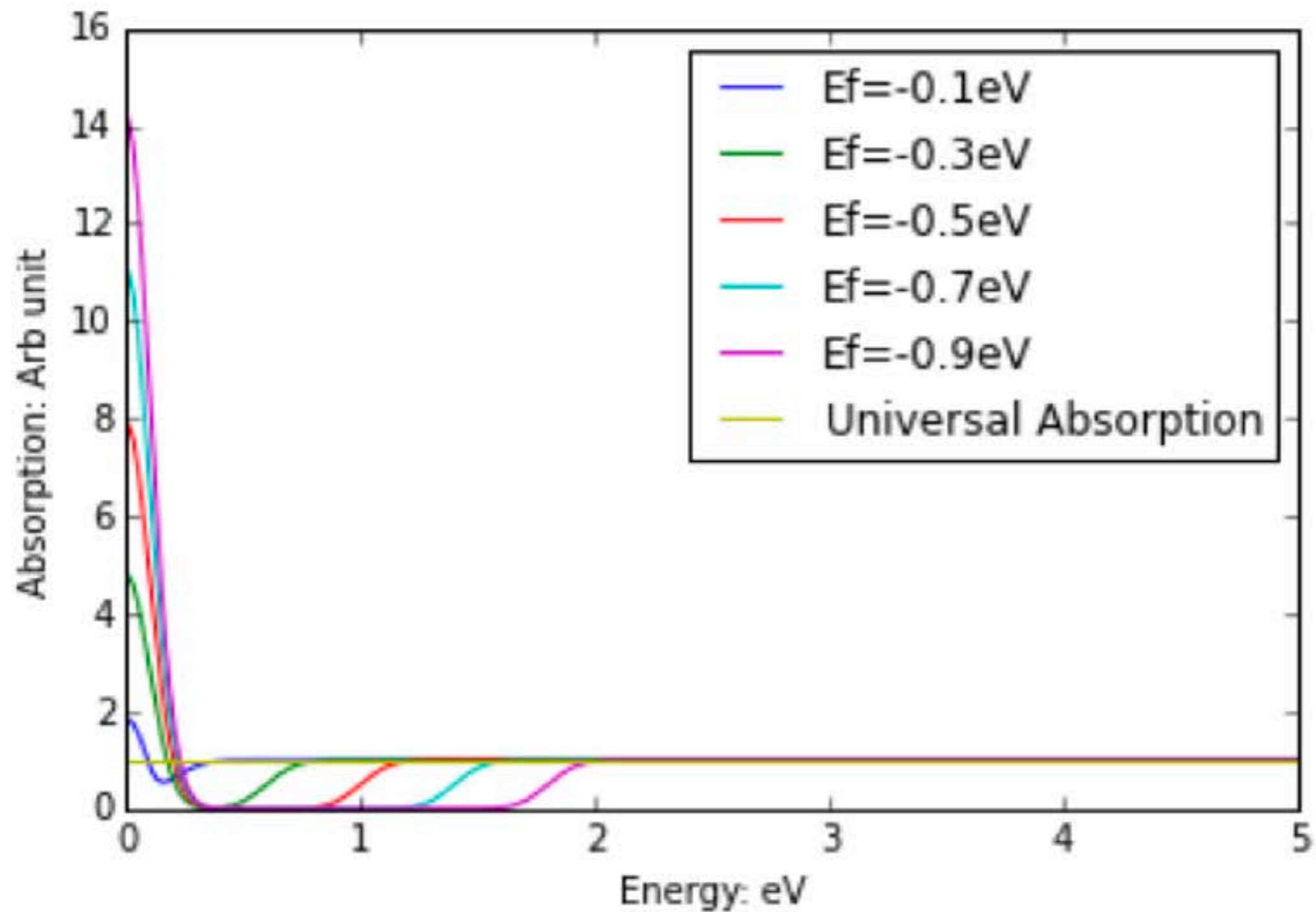
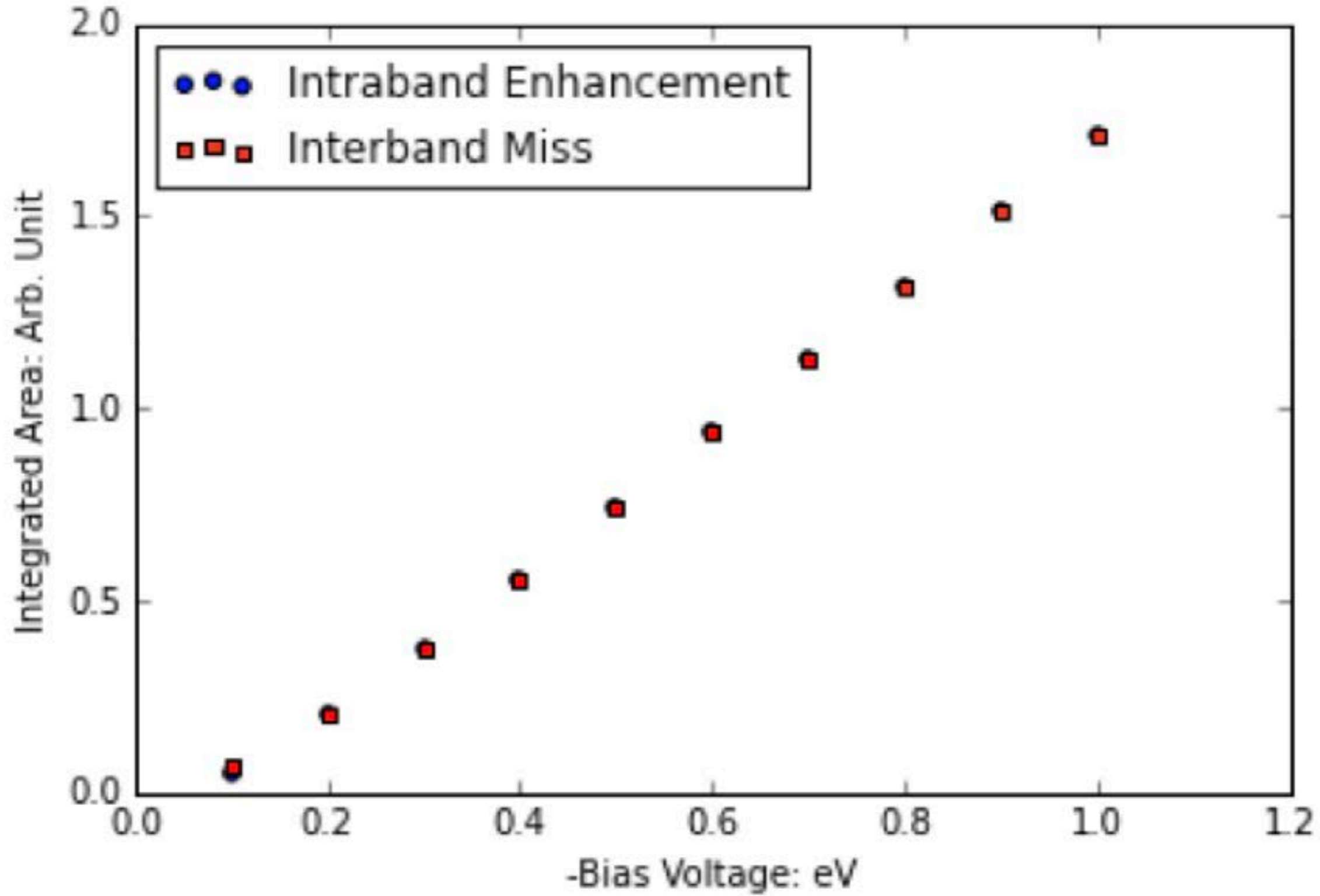


Figure 9: Infrared and far infrared absorption when the Fermi level is shifted down by different biases: The plot shows the dip of absorption in the infrared

Theory using phononless intraband absorption



D and 2D Stokes, anti-Stokes anomalies

Solid: Stokes

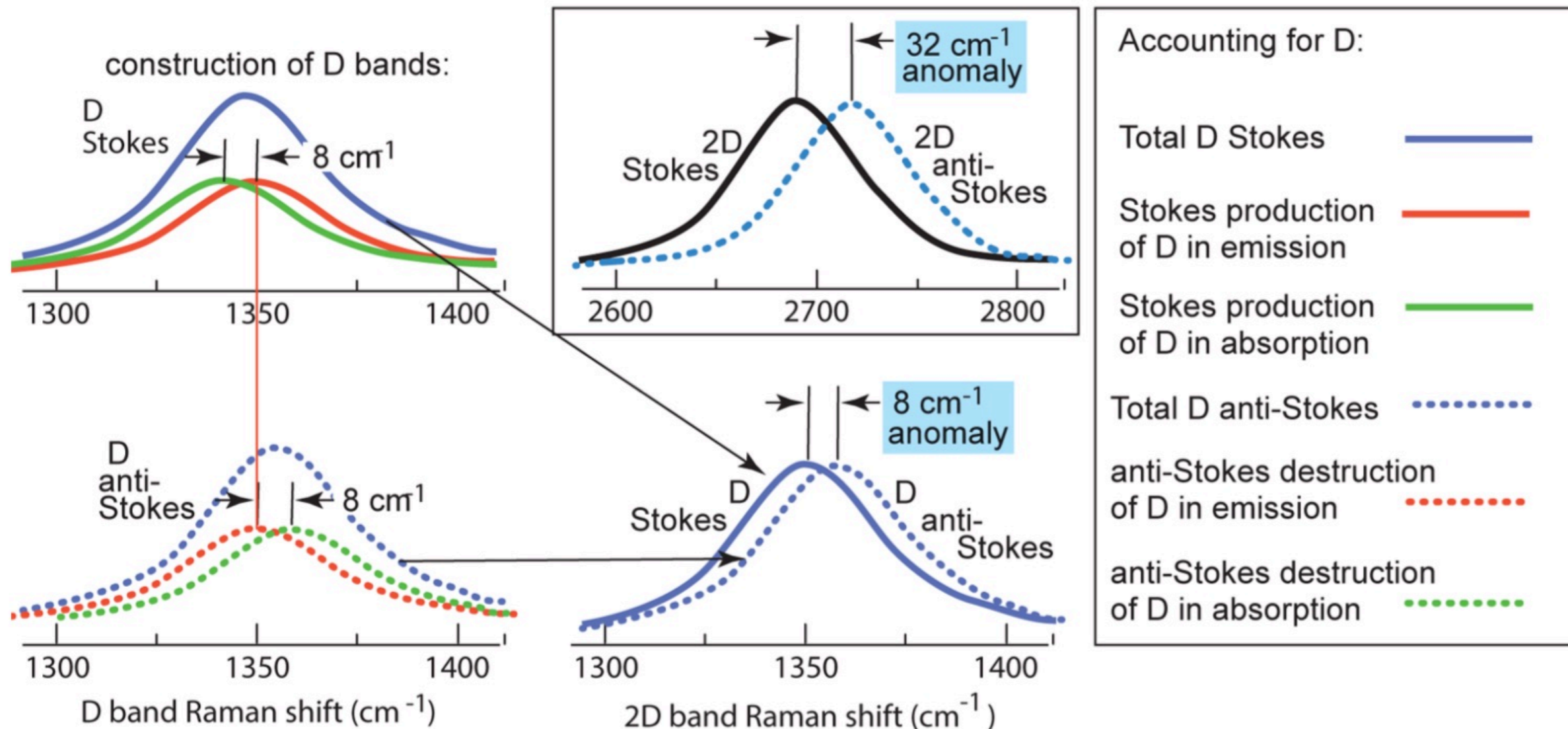
Anti-Stokes bands are reflected

The 2D scale spans twice

Dotted: anti-Stokes

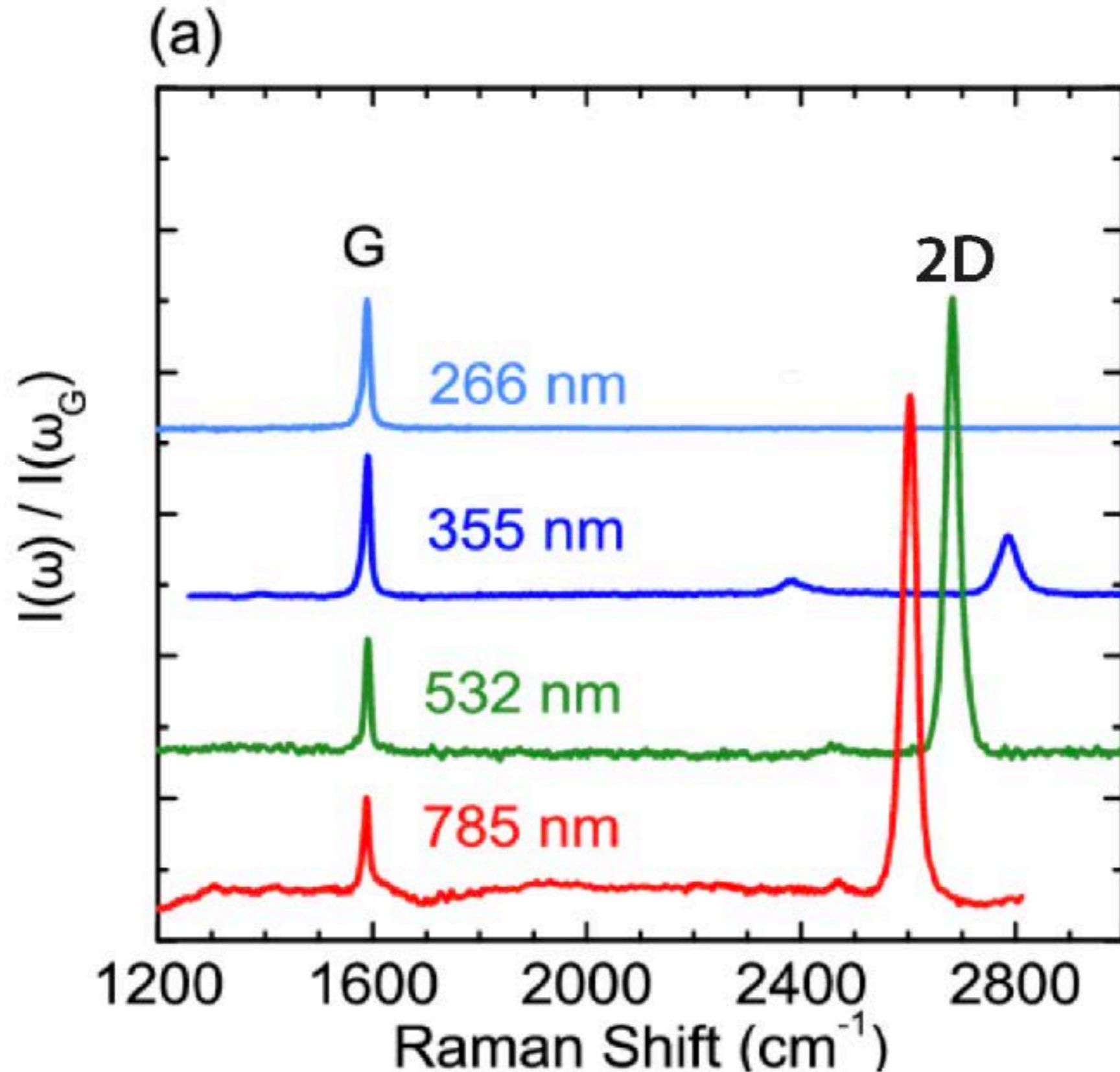
about the Rayleigh line.

the range of D.



32 cm⁻¹ 2D anomaly: -8 twice making 2D Stokes,
+8 twice making 2D anti-Stokes

Disappearing act of 2D in the UV



Syahril Siregar
Tohoku University

2015

What justifies a blackbody emission?

Even if the populations of electrons and hole were thermal at some T , why should they emit blackbody radiation?

(1) The absorption profiles are not constant

(2) Blackbody radiation is emitted by optically thick samples in equilibrium - graphene could not be any thinner

(3) What happened to specific electron - hole emission mechanisms?

(4) Assuming thermal populations, neither direct nor indirect mechanisms give blackbody radiation

Evidence of femtosecond relaxation?

No - sliding transitions modulate this absorption profile in 0 time

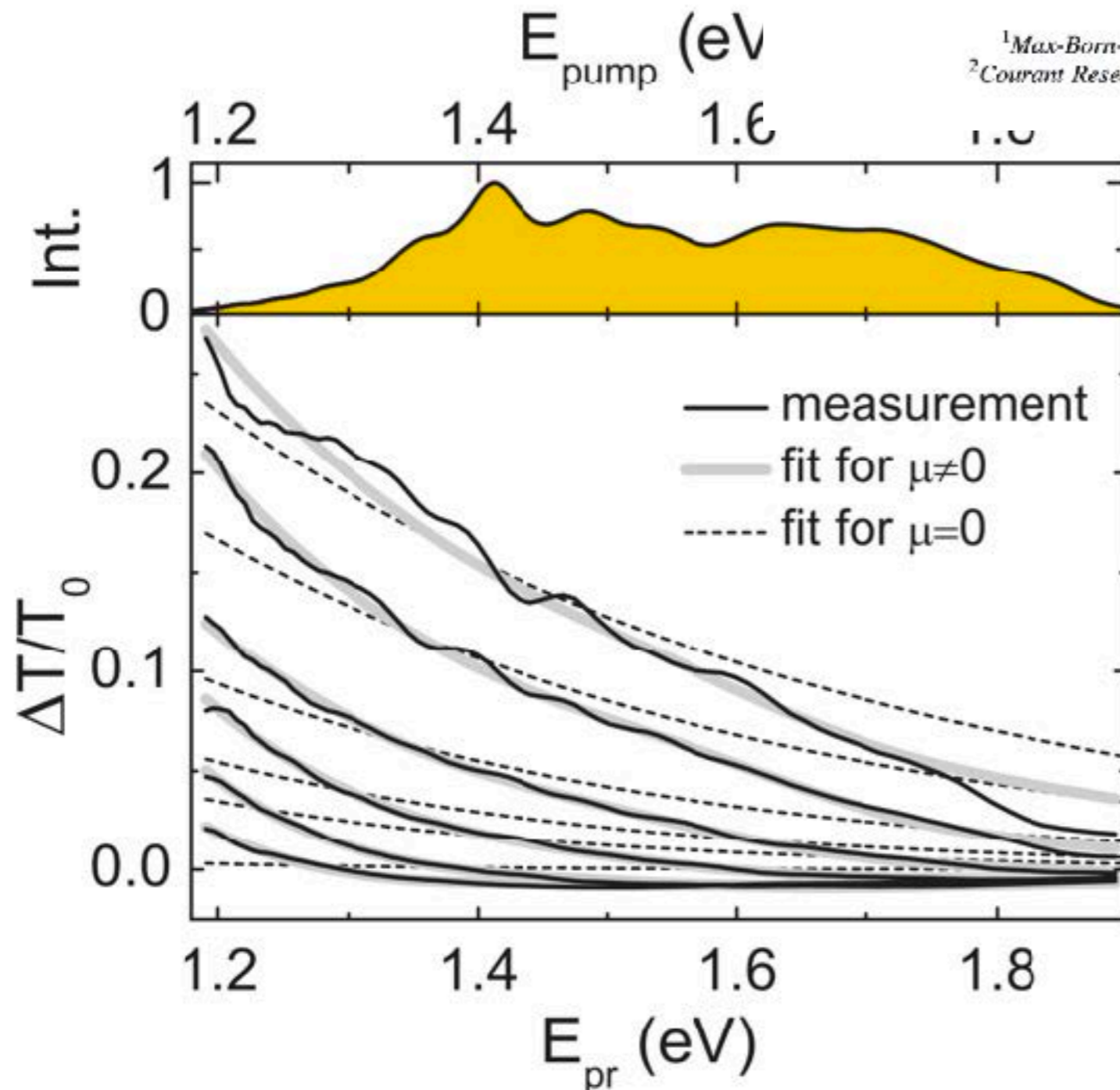
Ultrafast Carrier Dynamics in Graphite

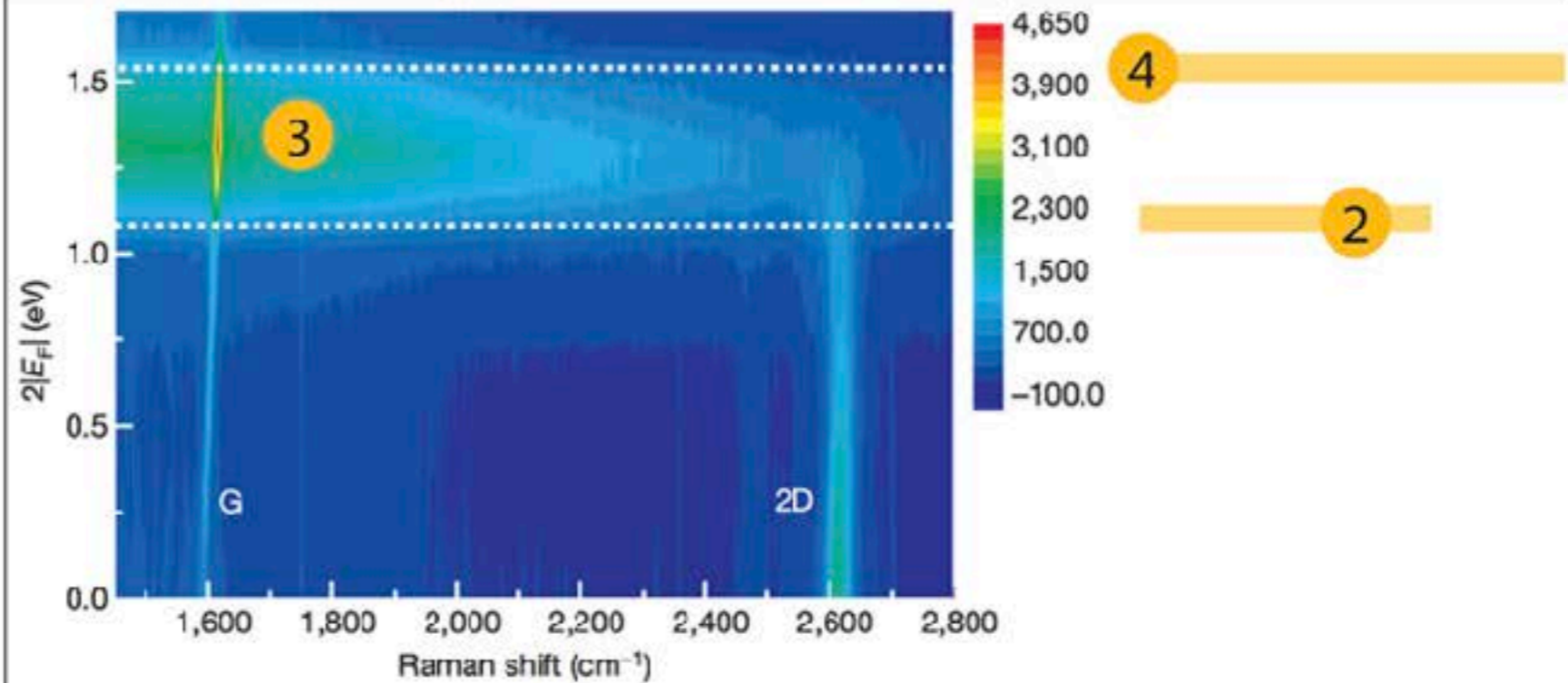
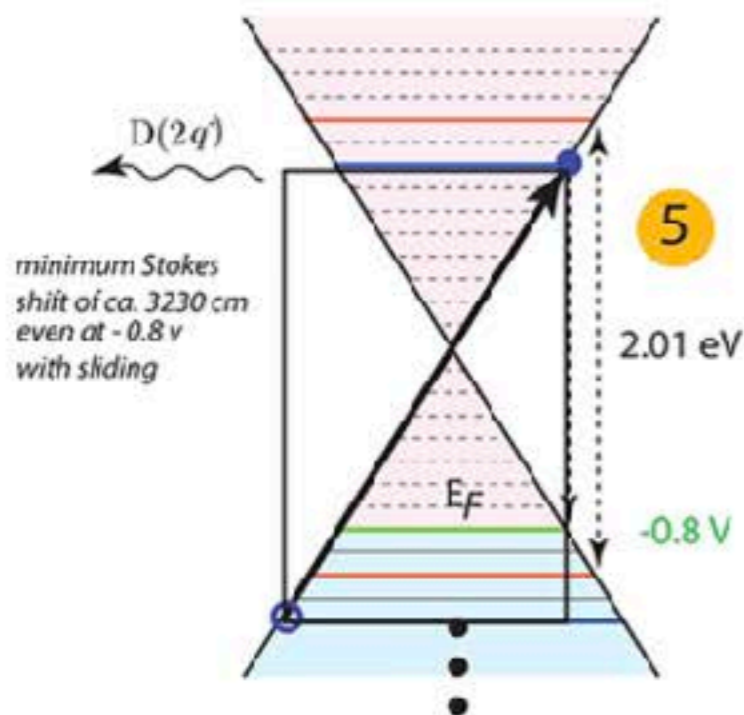
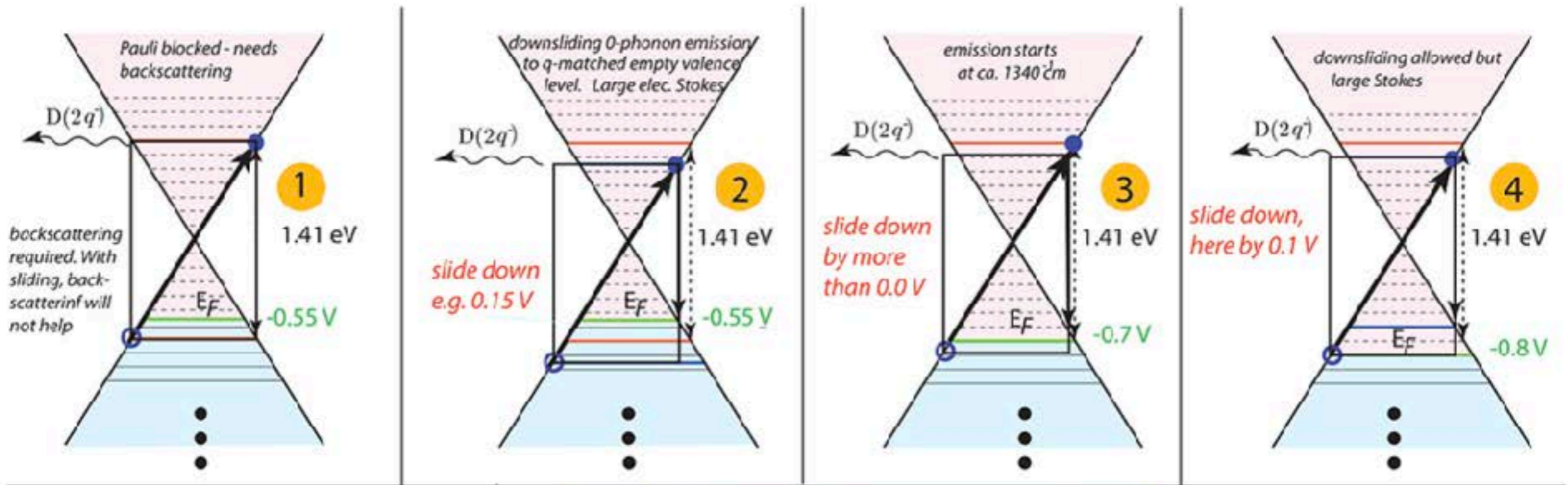
Markus Breusing,¹ Claus Ropers,^{1,2,*} and Thomas Elsaesser¹

¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany

²Courant Research Center Nano-Spectroscopy and X-Ray Imaging, University of Göttingen, Germany

(Received 5 September 2008; published 27 February 2009)

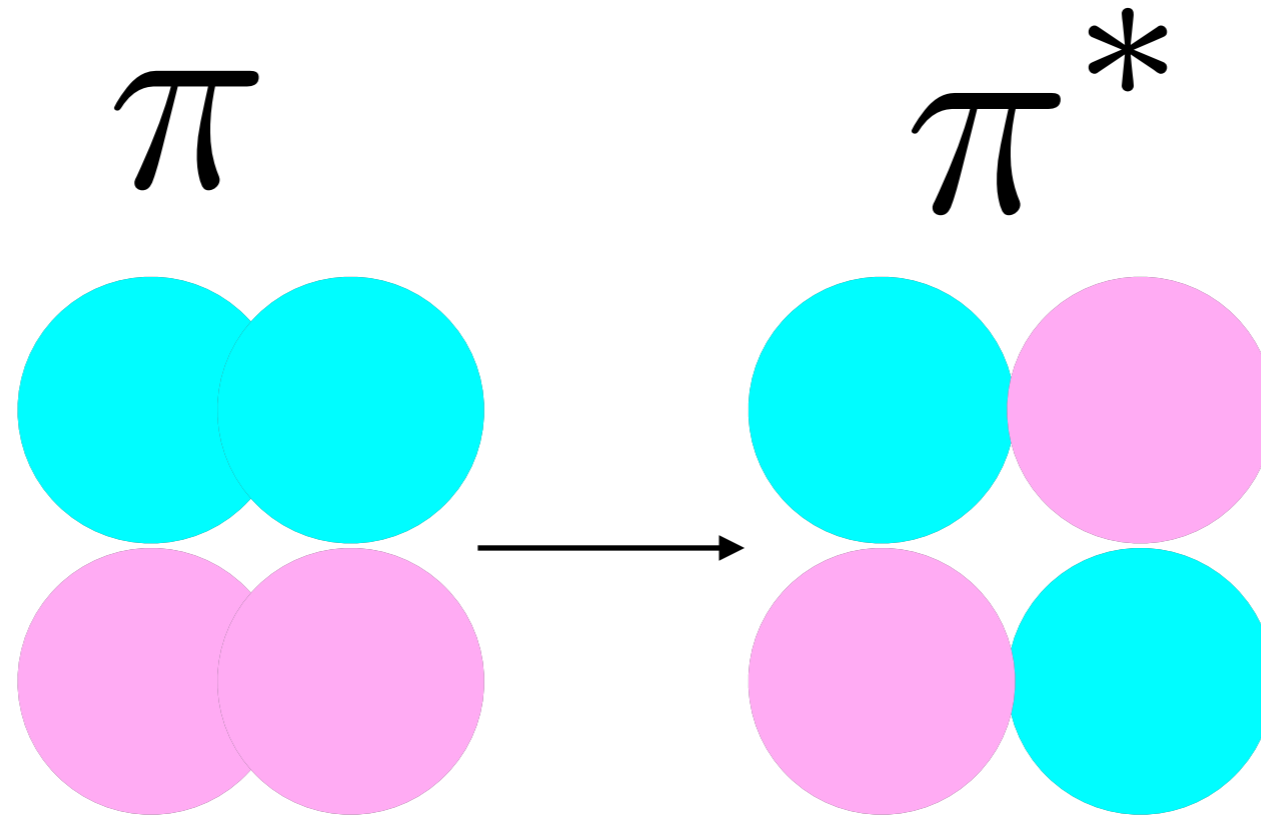




Mystery

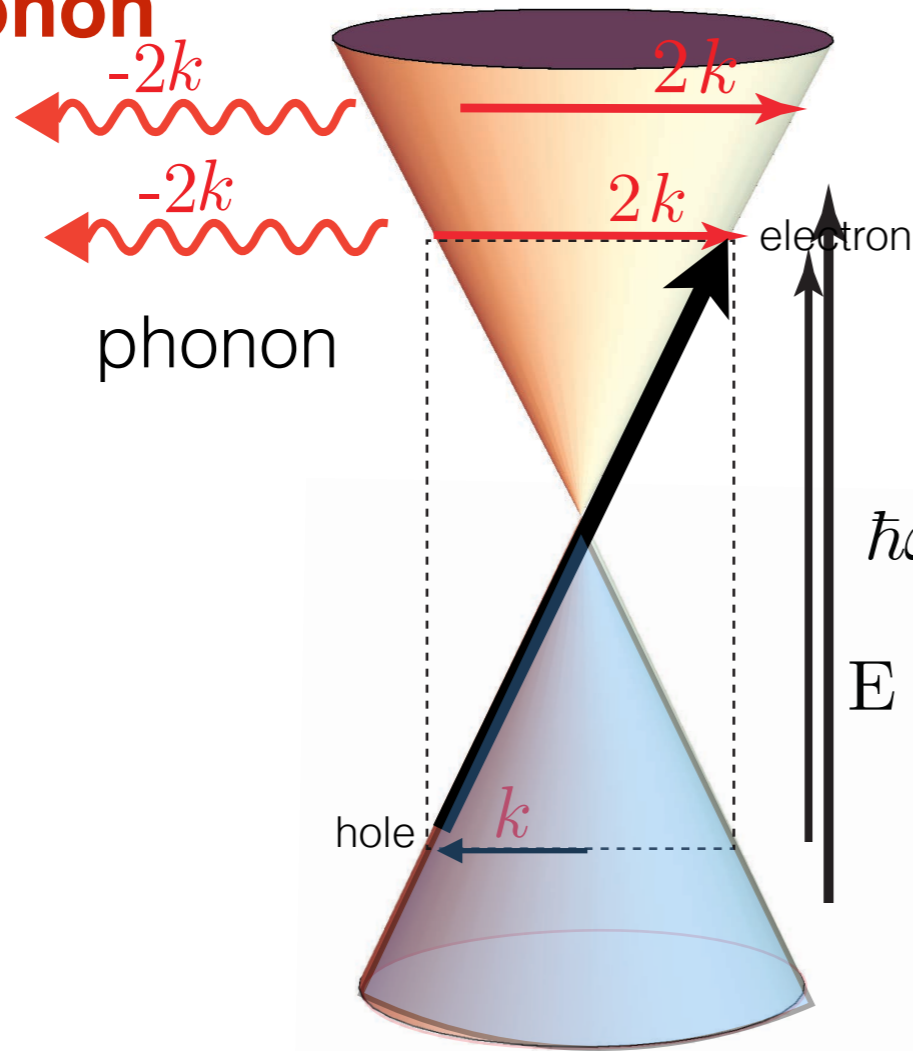
The coherent sum of all one-photon sliding transitions (each is a coherent amplitude) is a kind of anti-exciton, with momentum

distance dependence of absorption
probability



The same phonon is produced for any amount of collinear sliding on linear cones

same phonon



This happens instantly!

No waiting - caused by transition moment

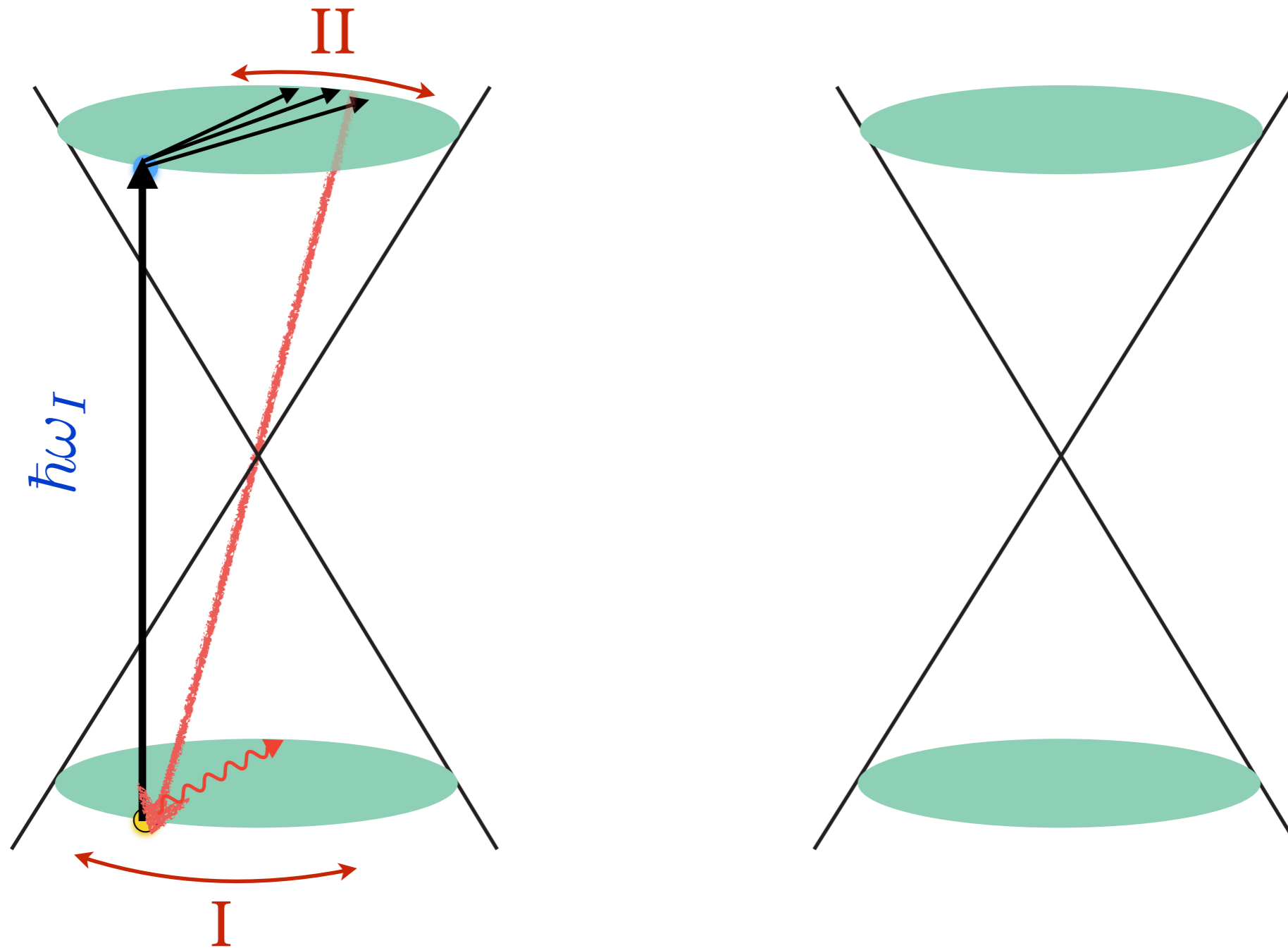
electronic transition
diminished to "pay"
for resonant phonon
creation

Graphene Absorption and Raman Spectroscopy

1. An infrared and THz absorption problem is identified and solved with new physics

1. VIS-UV absorption spectrum is partially indirect in nature

D phonon production in emission



KHD

Stokes G phonon
produced at absorption

recombination

