# Cooling quasiparticles in $A_3C_{60}$ fullerides by excitonic mid-infrared absorption


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ECRYS 2017


with

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arXiv:1704.05613

# Outline

- Brief remark about superconductivity in $A_3C_{60}$
- Our view on the experimental evidences of light-enhanced $T_c$: the key actor is the excitation responsible of the anomalous mid-IR optical behaviour
- Molecular spectrum of $C_{60}^{3-}$: strongly-bound odd-parity spin-triplet excitons
- Role of those excitons in the mid-IR response and in the light-enhanced superconductivity

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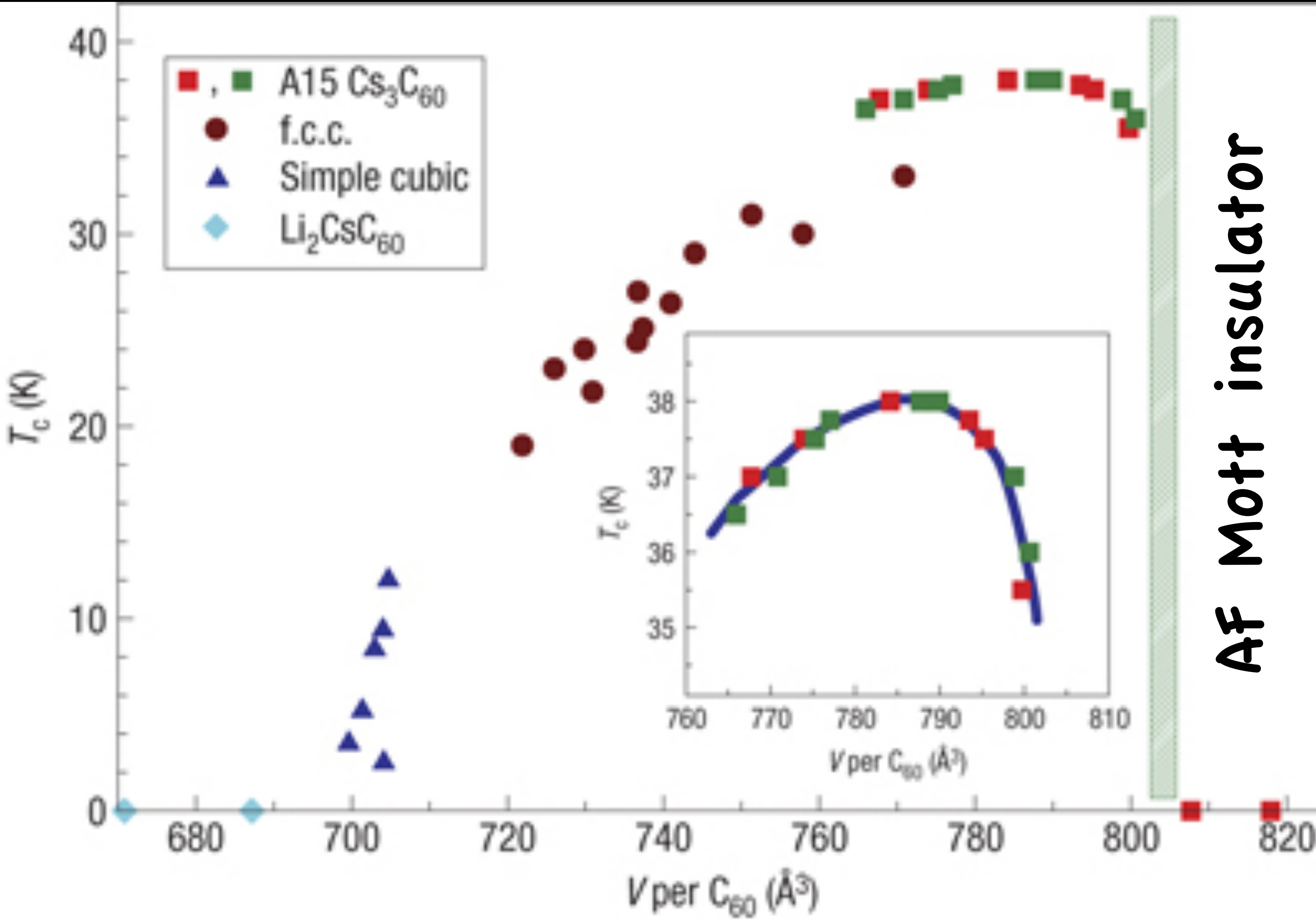
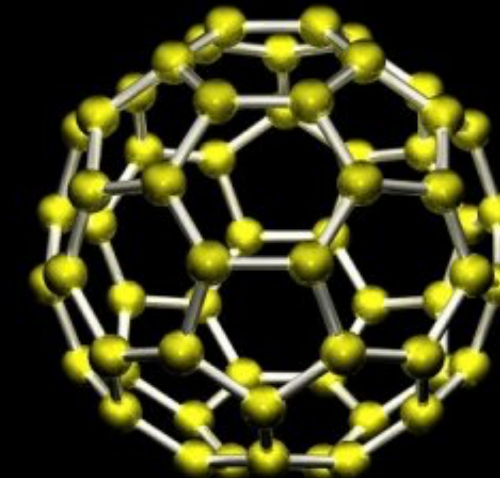
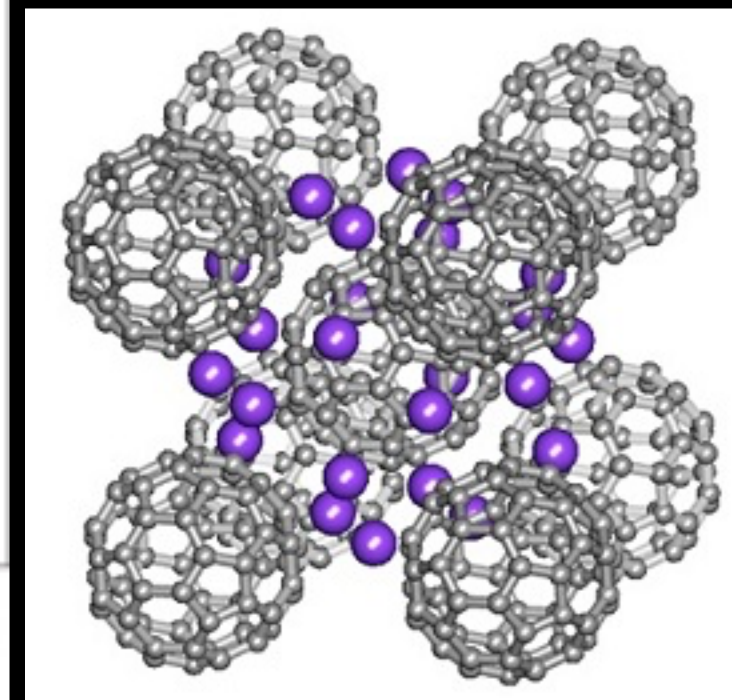




- pairing mechanism: molecular vibrations of $H_g$ symmetry Jahn-Teller coupled to electrons
- Jahn-Teller strengthened by correlations rather than weakened

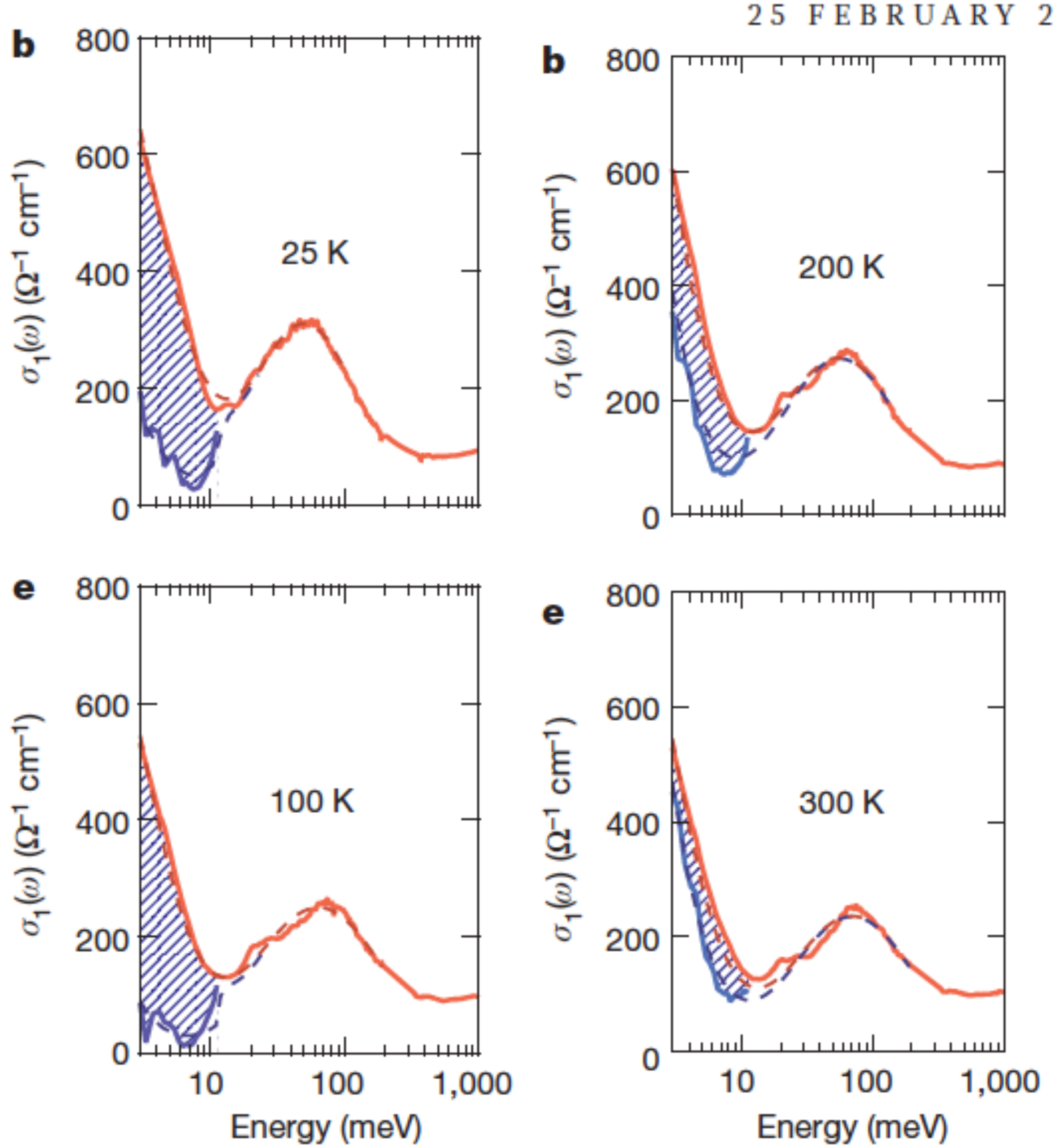
# LETTER

doi:10.1038/nature16522

## Possible light-induced superconductivity in $K_3C_{60}$ at high temperature

M. Mitrano[1], A. Cantaluppi[1,2], D. Nicoletti[1,2], S. Kaiser[1], A. Perucchi[3], S. Lupi[4], P. Di Pietro[3], D. Pontiroli[5], M. Riccò[5], S. R. Clark[1,6,7], D. Jaksch[7,8] & A. Cavalleri[1,2,7]

25 FEBRUARY 2016 | VOL 530 | NATURE | 461

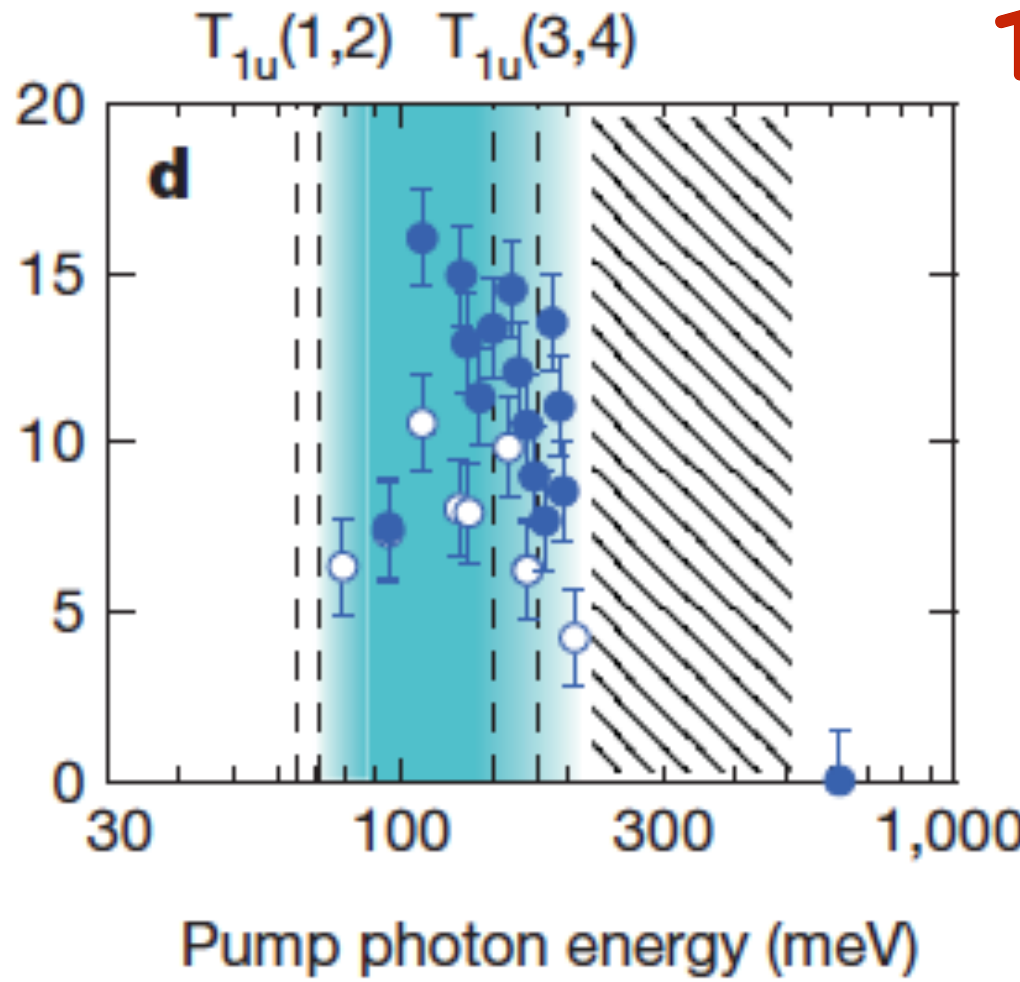



pump-probe experiment: pump pulse of 300 fs with MIR frequency; optical probe

transient reduction of $\sigma_1$ with respect to equilibrium that extends up to 200 K, twenty times the equilibrium Tc ≈ 20K, and much higher than $T_c^{MAX}$ ≈ 40K !!!

# original interpretation:

$$\int_{3\,\mathrm{meV}}^{10\,\mathrm{meV}} d\omega\ |\Delta\sigma_1(\omega)|$$




T = 25 K

○ 0.4 mJ/cm²

● 1.1 mJ/cm²

the pump frequencies where a superconducting-like signal is observed seem to accumulate around the $T_{1u}$ vibrational modes ⇨ excitation of those modes is thus responsible of the phenomenon

# all theoretical explanations assume the phonon-driven interpretation and argue for a light-enhanced effective pairing strength

PHYSICAL REVIEW B **94**, 155152 (2016)

**Enhancing superconductivity in $A_3C_{60}$ fullerides**

Minjae Kim,[1,2,*] Yusuke Nomura,[1] Michel Ferrero,[1,2] Priyanka Seth,[2,3] Olivier Parcollet,[2,3] and Antoine Georges[1,2,4]

PHYSICAL REVIEW B **96**, 014512 (2017)

**Theory of parametrically amplified electron-phonon superconductivity**

Mehrtash Babadi,[1,2,*] Michael Knap,[3] Ivar Martin,[4] Gil Refael,[1] and Eugene Demler[5]

PHYSICAL REVIEW B **96**, 064515 (2017)

**Nonequilibrium superconductivity in driven alkali-doped fullerides**

Giacomo Mazza[1,2] and Antoine Georges[1,2,3]

PHYSICAL REVIEW B **94**, 214504 (2016)

**Dynamical Cooper pairing in nonequilibrium electron-phonon systems**

Michael Knap,[1] Mehrtash Babadi,[2] Gil Refael,[2] Ivar Martin,[3] and Eugene Demler[4]

PHYSICAL REVIEW B **96**, 045125 (2017)

**Nonequilibrium steady states and transient dynamics of conventional superconductors under phonon driving**

Yuta Murakami,[1] Naoto Tsuji,[2] Martin Eckstein,[3] and Philipp Werner[1]

nature physics ARTICLES
PUBLISHED ONLINE: 30 JANUARY 2017 | DOI: 10.1038/NPHYS4024

**Transient superconductivity from electronic squeezing of optically pumped phonons**

Dante M. Kennes[1†], Eli Y. Wilner[1†], David R. Reichman[2] and Andrew J. Millis[1*]

PHYSICAL REVIEW B **93**, 144506 (2016)

**Theory of light-enhanced phonon-mediated superconductivity**

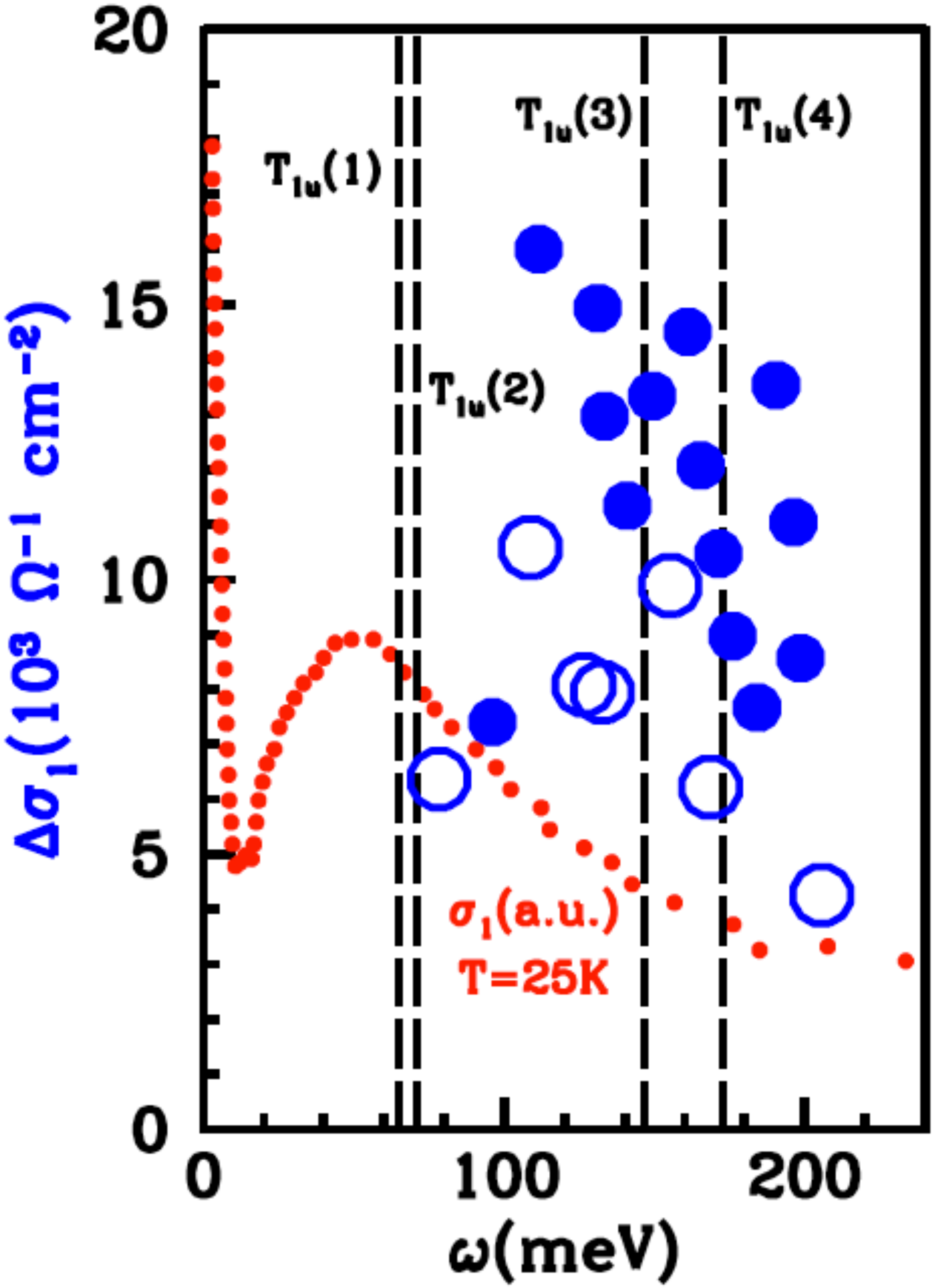
M. A. Sentef,[1,2,*] A. F. Kemper,[3,4] A. Georges,[5,6,7] and C. Kollath[1]

PHYSICAL REVIEW B **95**, 205111 (2017)

**Light-enhanced electron-phonon coupling from nonlinear electron-phonon coupling**

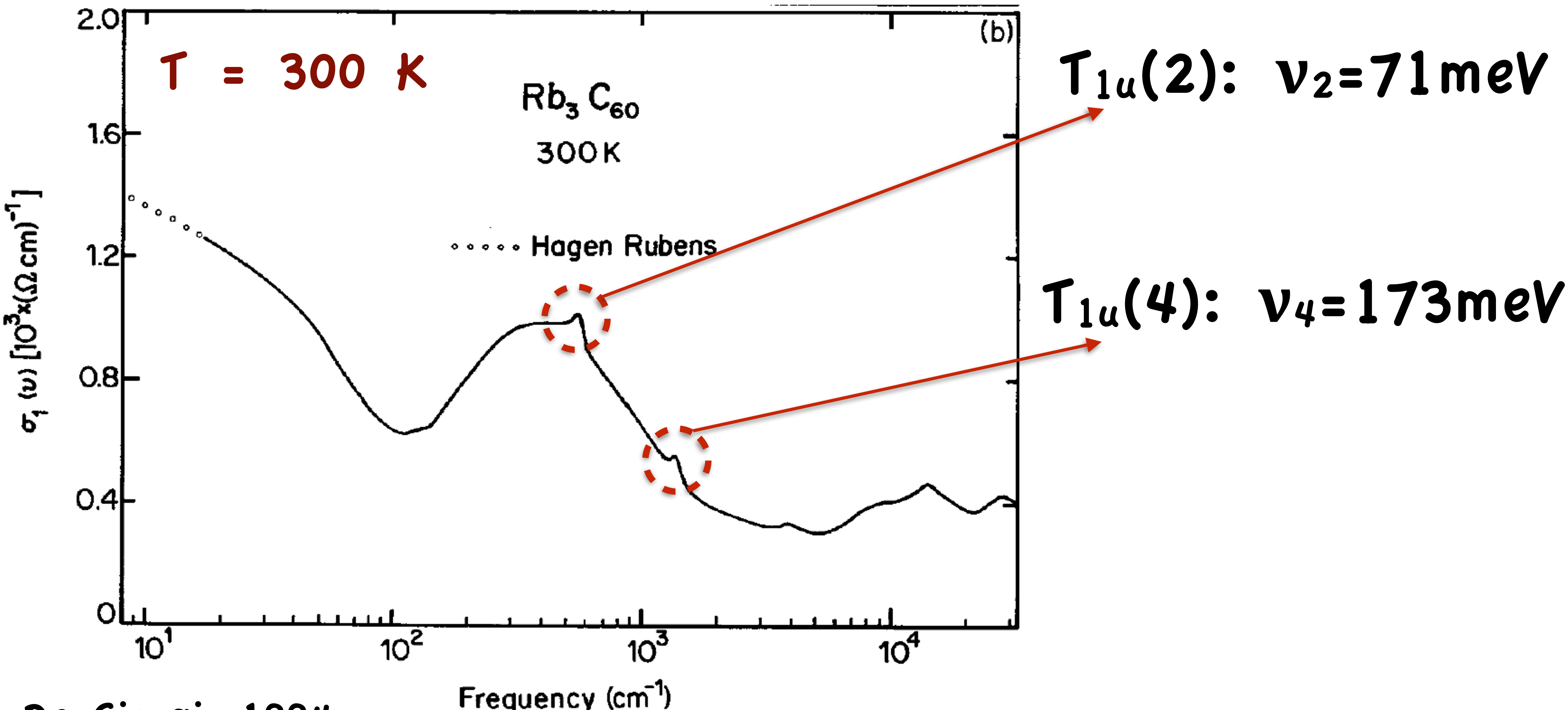
M. A. Sentef[*]

# simple-minded theorist's interpretation:



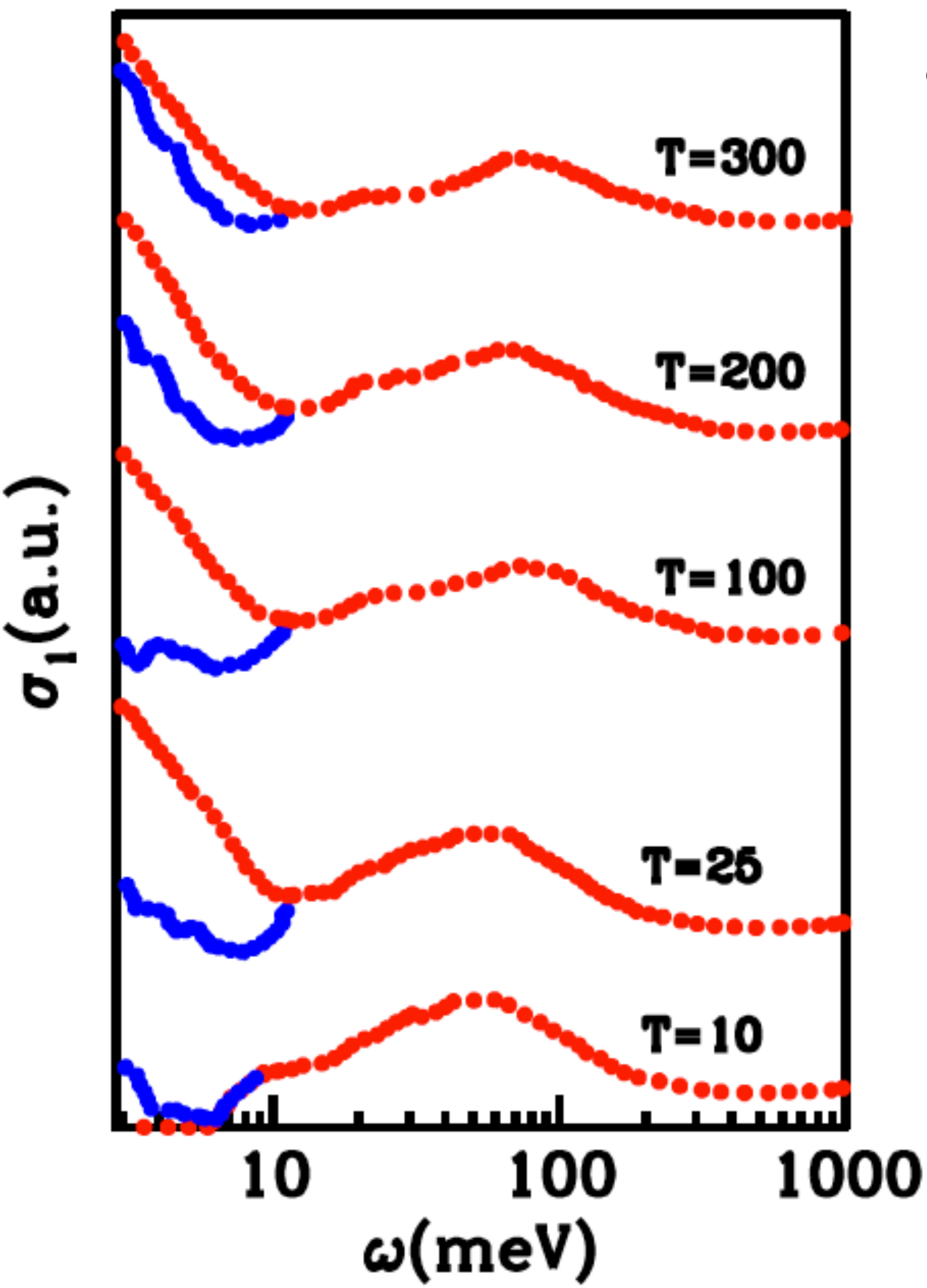

(1)

the phenomenon is correlated with the still unexplained MIR absorption peak at 55 meV rather than with the $T_{1u}$ modes




De Giorgi, 1994

$T_{1u}$ contribution to optical absorption is indeed negligibly small equilibrium — 1ps after irradiation

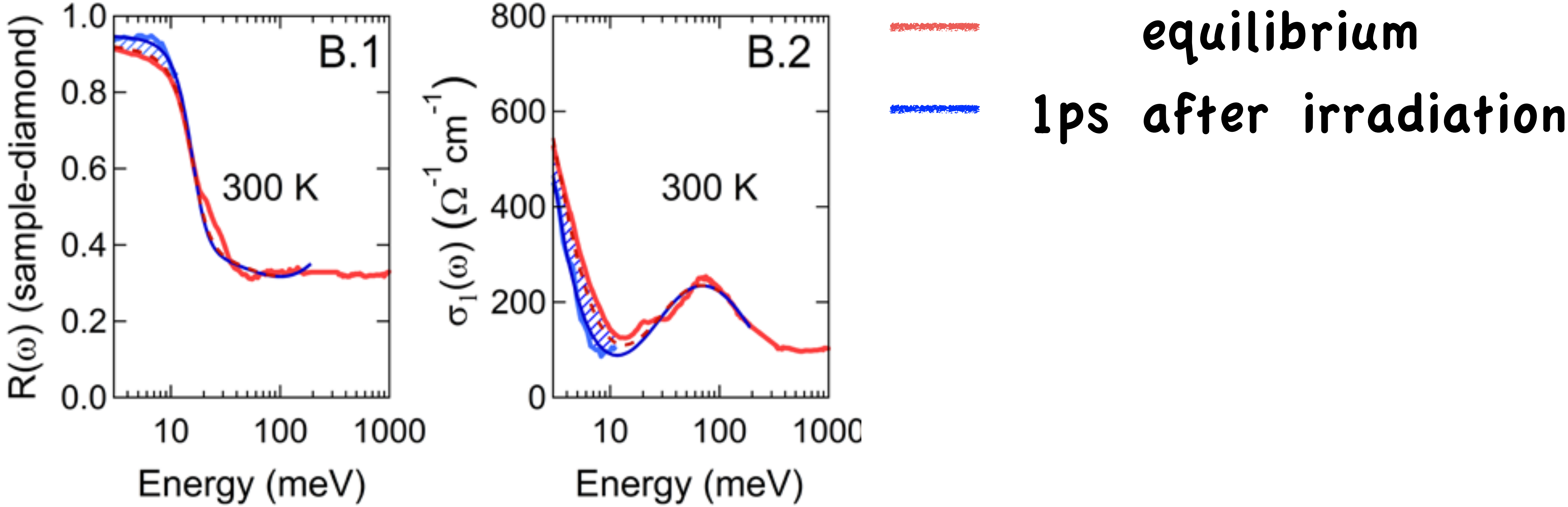



- in $K_3C_{60}$ the transition occurs by gap filling rather than gap closing

**(2)**

the laser cleans out thermal excitations from a pre-existing gap rather than increasing the effective pairing strength

⇨ it effectively cools down the system




indeed, even though at T = 300 K the optical response cannot be fit anymore by a superconducting one, still the low frequency reflectivity transiently increases as if the temperature were lower

## change of perspective:

(1) the phenomenon is due to the excitation responsible of the mysterious MIR absorption peak observed in equilibrium at 55 meV

(2) the laser pulse transiently cools down quasiparticles, eventually below the equilibrium $T_c$

let us start from

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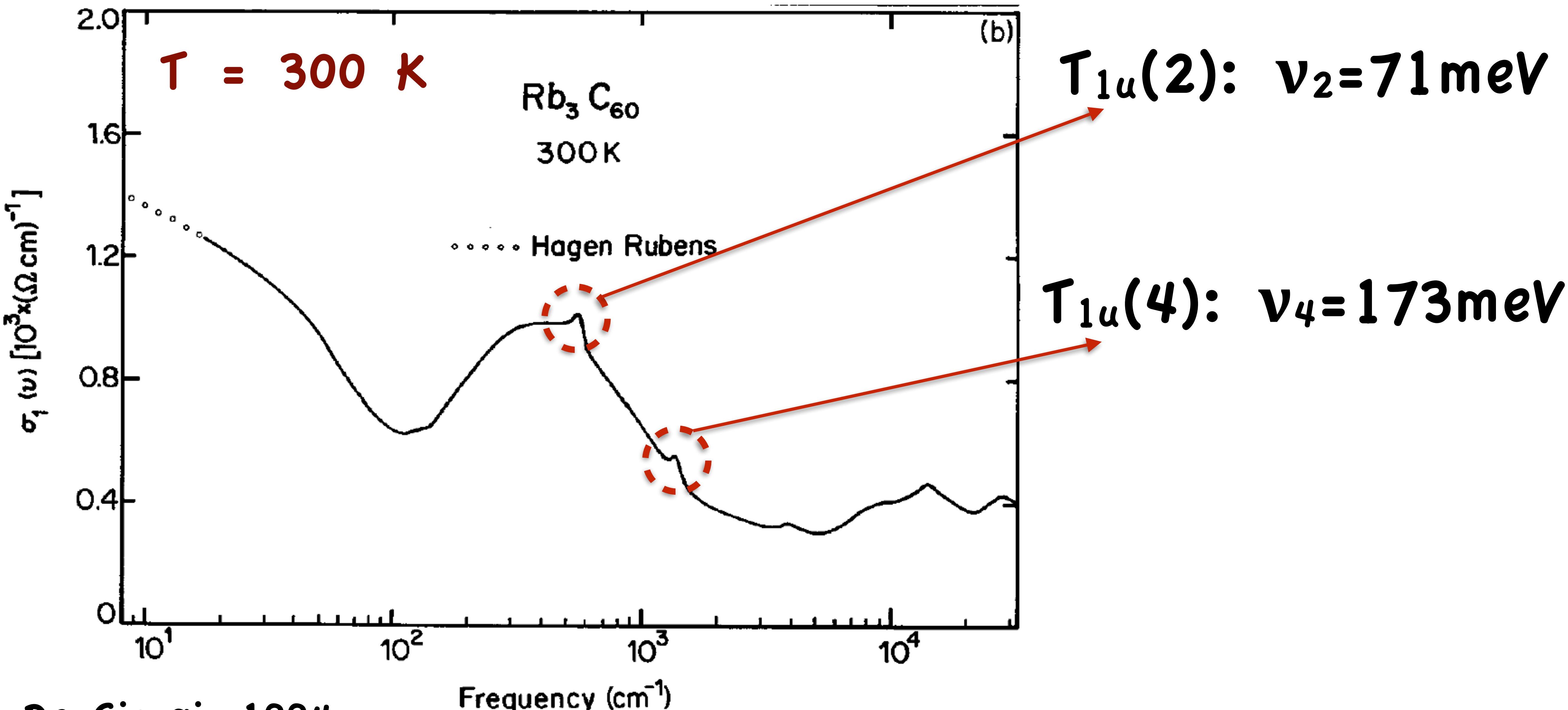
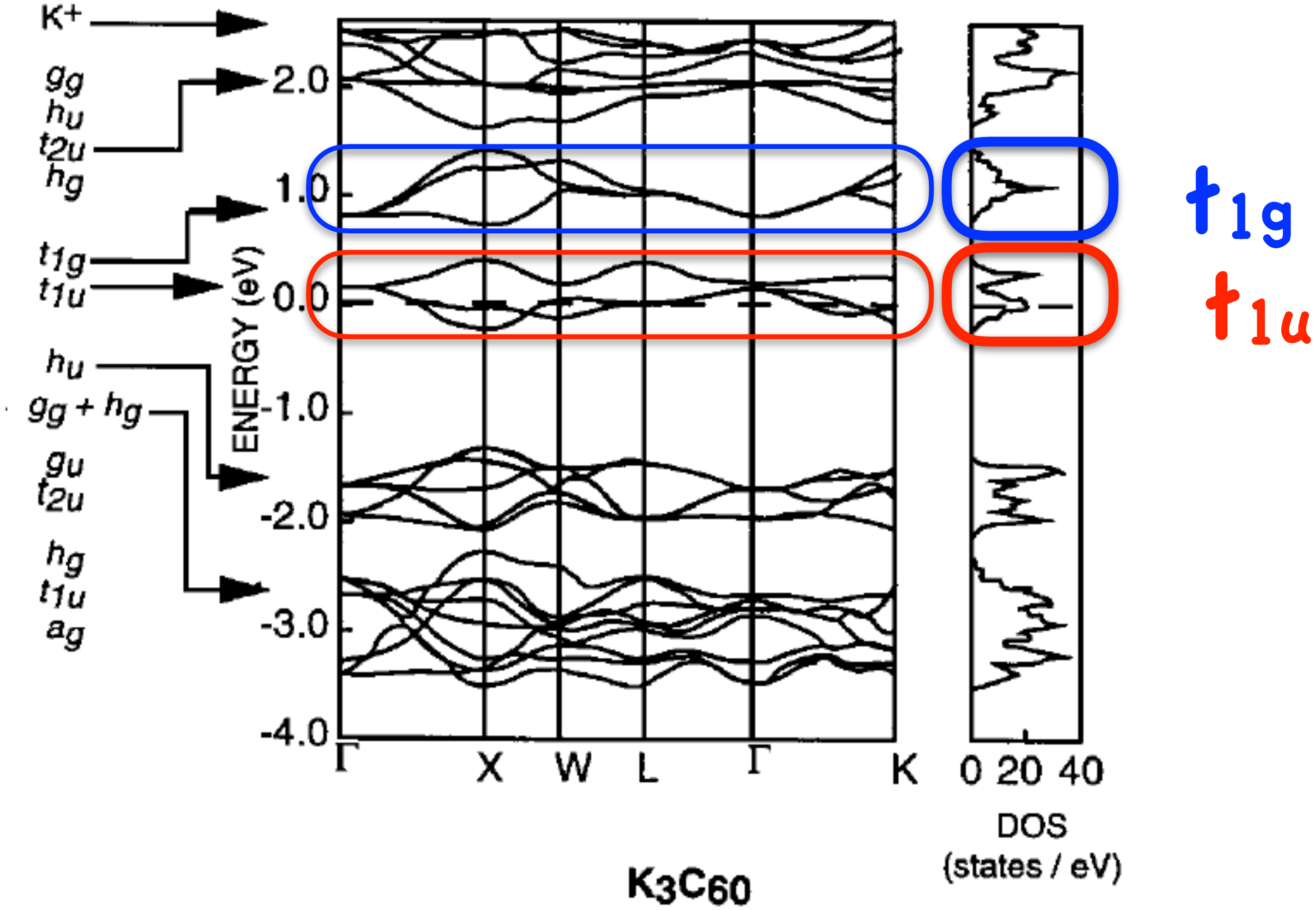


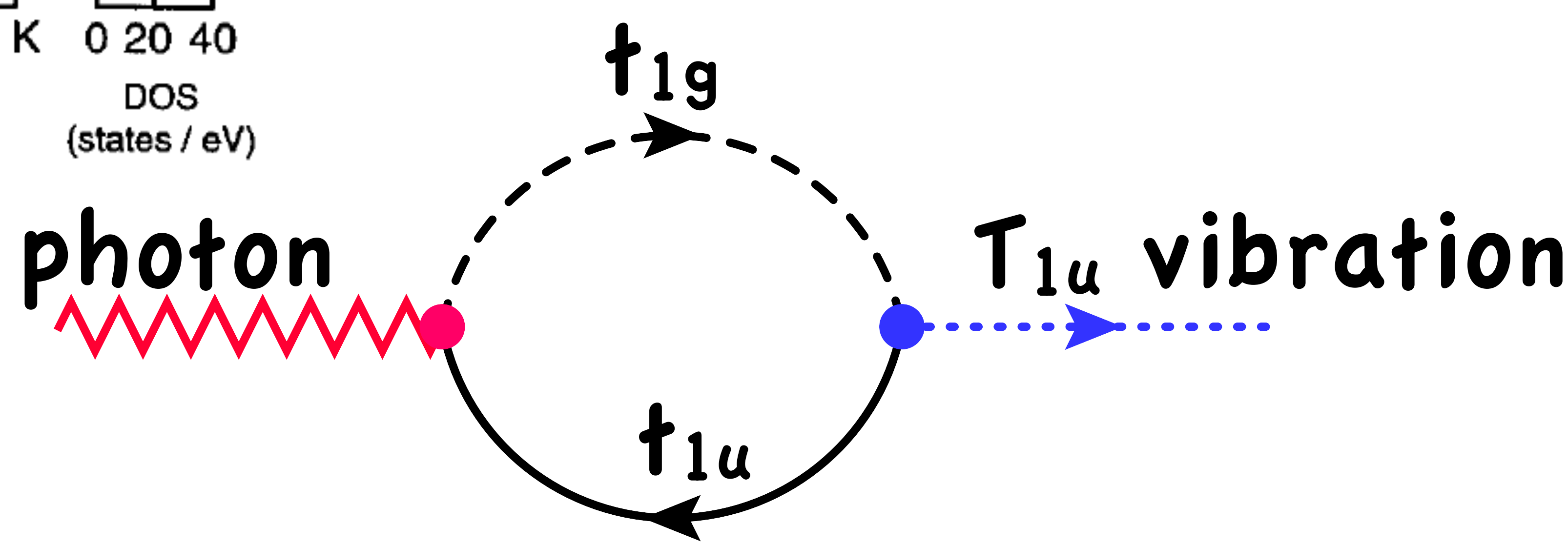

De Giorgi, 1994

how do $T_{1u}$ modes partecipate at all to absorption despite they are uncharged?

# Rice & Choi theory (1992)



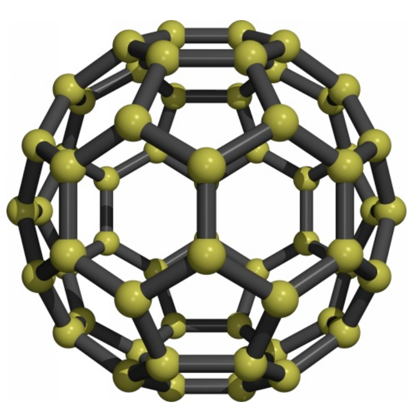

dipole allowed transition

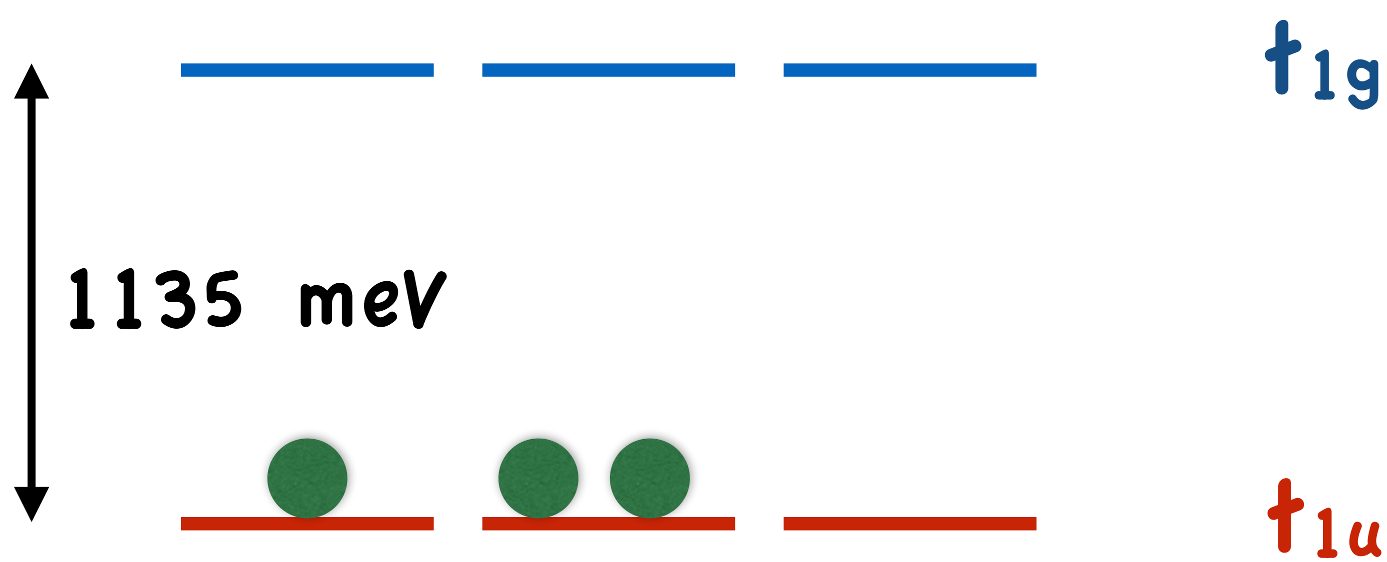



the photon can decay into a $T_{1u}$ vibration
via a virtual $t_{1u} \rightarrow t_{1g}$ transition

the whole process is intra-molecular!

# Let us therefore study the isolated $C_{60}^{3-}$ molecule taking into account both $(t_{1u})^3$ and $(t_{1u})^2(t_{1g})^1$ configurations





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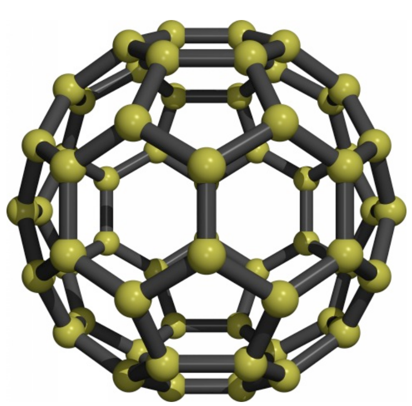
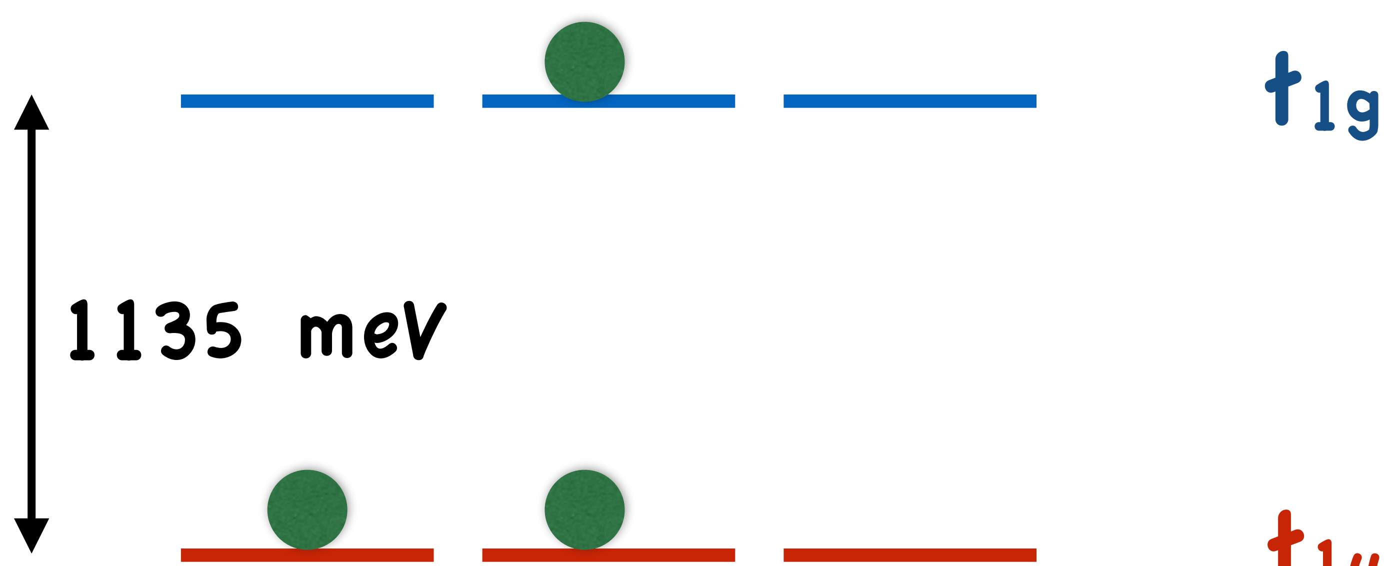
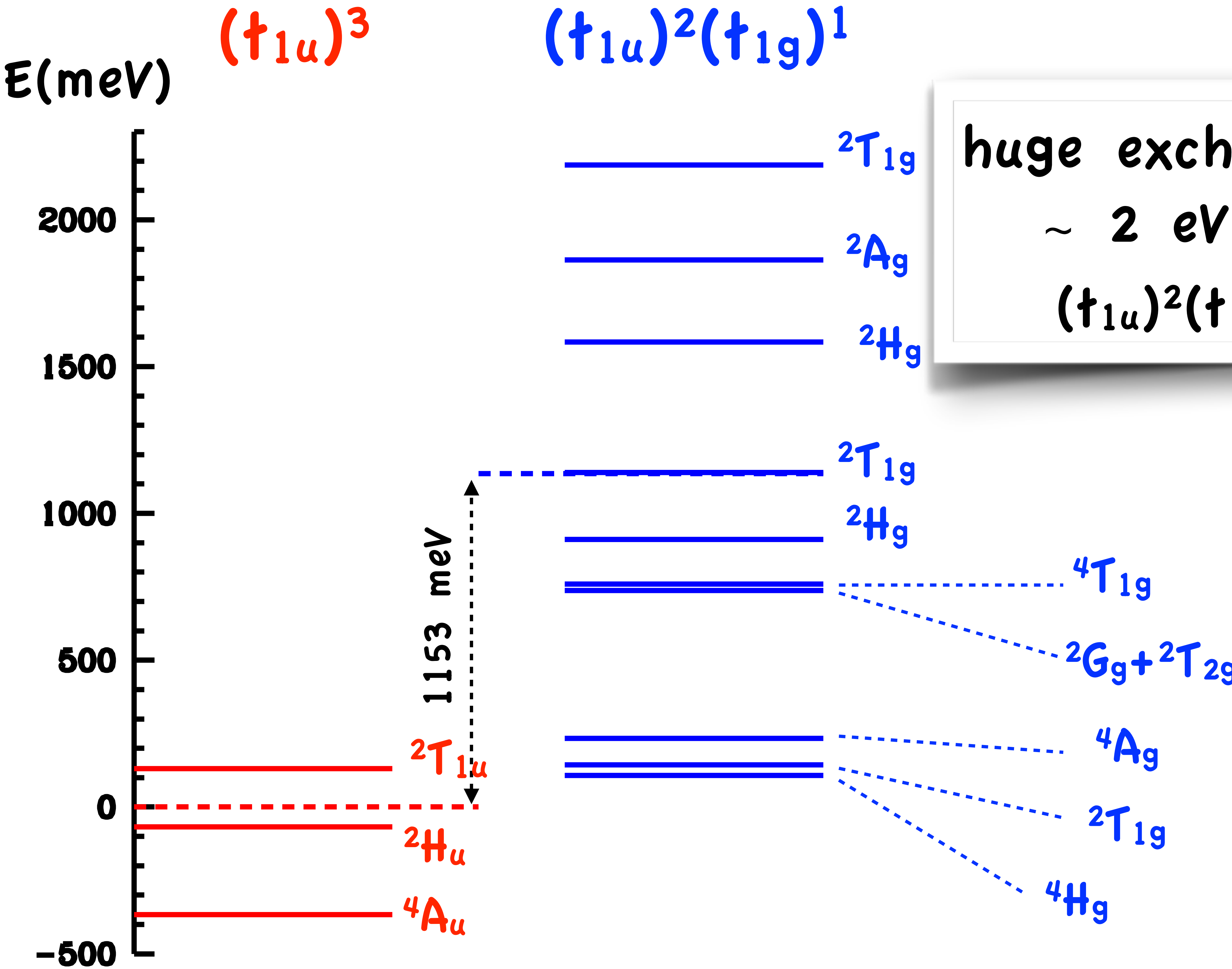




# Molecular spectrum without Jahn-Teller coupling

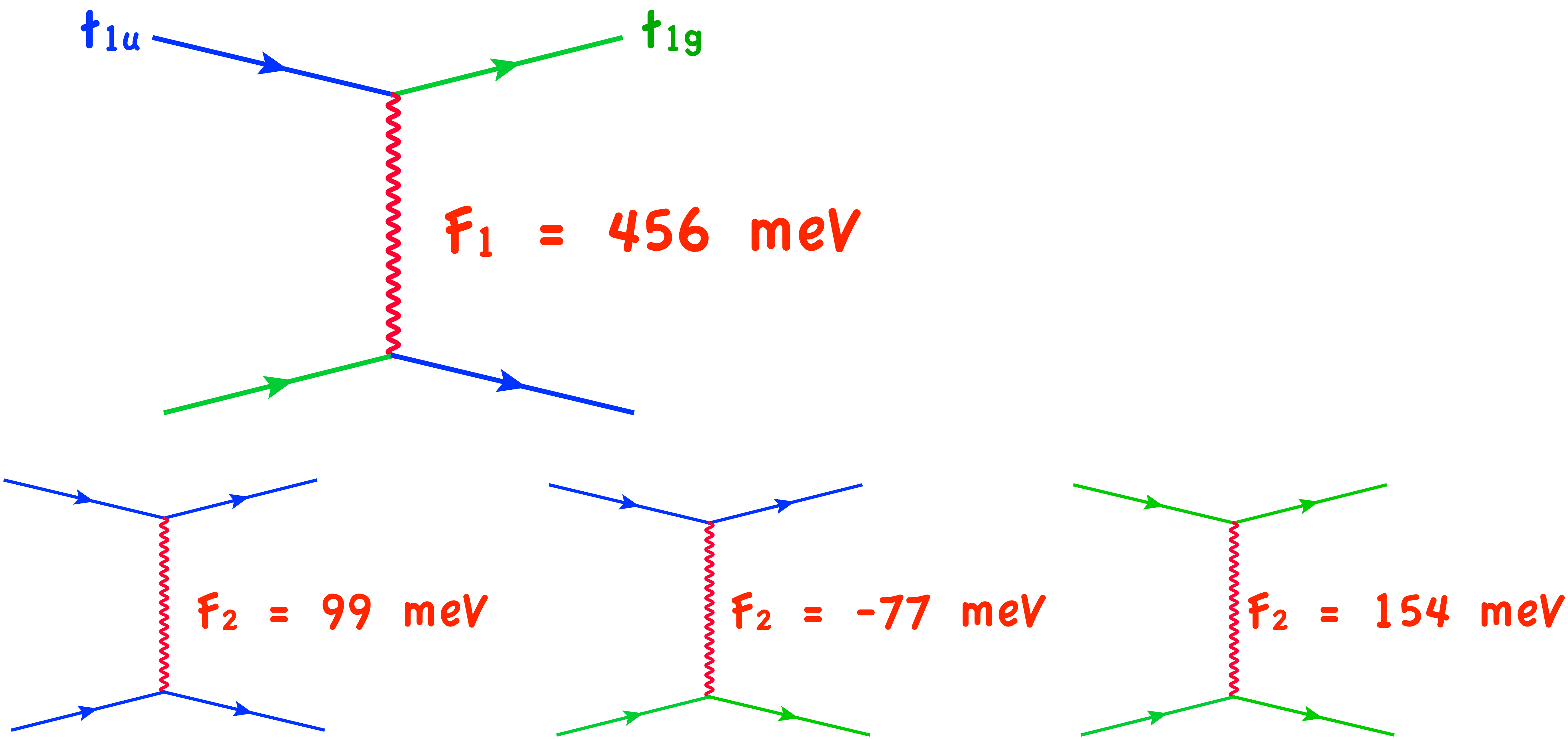
A.V. Nikolaev and K.H. Michel, J. Chem. Phys. 117, 4761 (2002)




huge exchange splitting
~ 2 eV of the 90
$(t_{1u})^2(t_{1g})^1$ states!

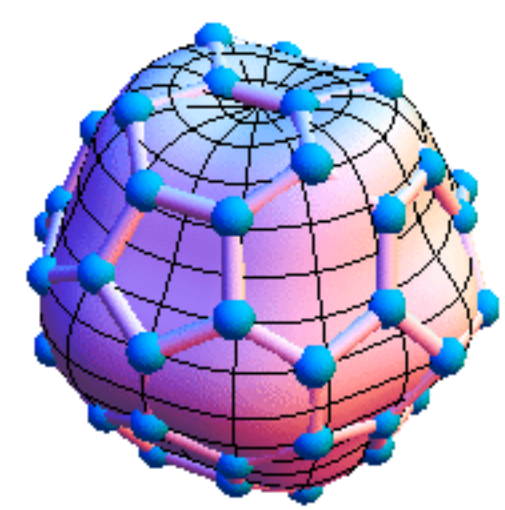
# Why such a huge exchange splitting?

- strong dipole-dipole interaction between $t_{1u}$ and $t_{1g}$ electrons acting within a subspace of 90 $(t_{1u})^2(t_{1g})^1$ states!



# ... but

we still need to include the crucial Jahn-Teller coupling between the quadrupole moments of the $t_{1u}$ and $t_{1g}$ electrons and the eight fivefold degenerate $H_g$ vibrational modes



- single-mode approximation:

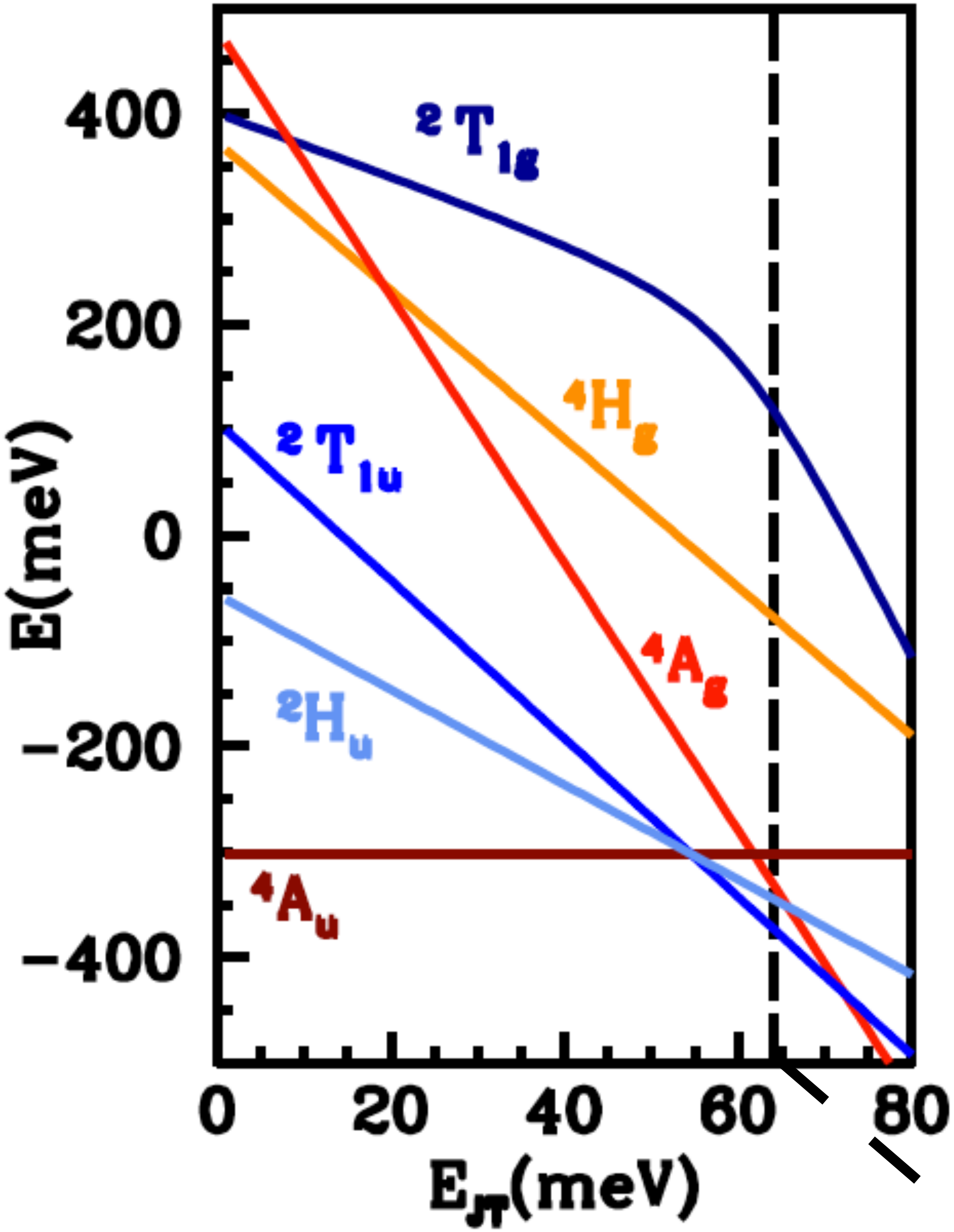
$$\mathcal{H}_{\mathrm{JT}} = -g_{\mathrm{JT}} \sum_{m=-2}^{2} (-1)^m \, x_{-m} \left( Q_m^u - Q_m^g \right) + \frac{\omega}{2} \sum_m (-1)^m \left( x_{-m} \, x_m + p_{-m} \, p_m \right)$$

- $Q_m^u \sim Y_{2m}$ — quadrupole operators of $t_{1u}$
- $Q_m^g \sim Y_{2m}$ — quadrupole operators of $t_{1g}$ (opposite to $t_{1u}$!)

## Jahn-Teller energy

$$E_{\mathrm{JT}} = \frac{g_{\mathrm{JT}}^2}{2\omega}$$

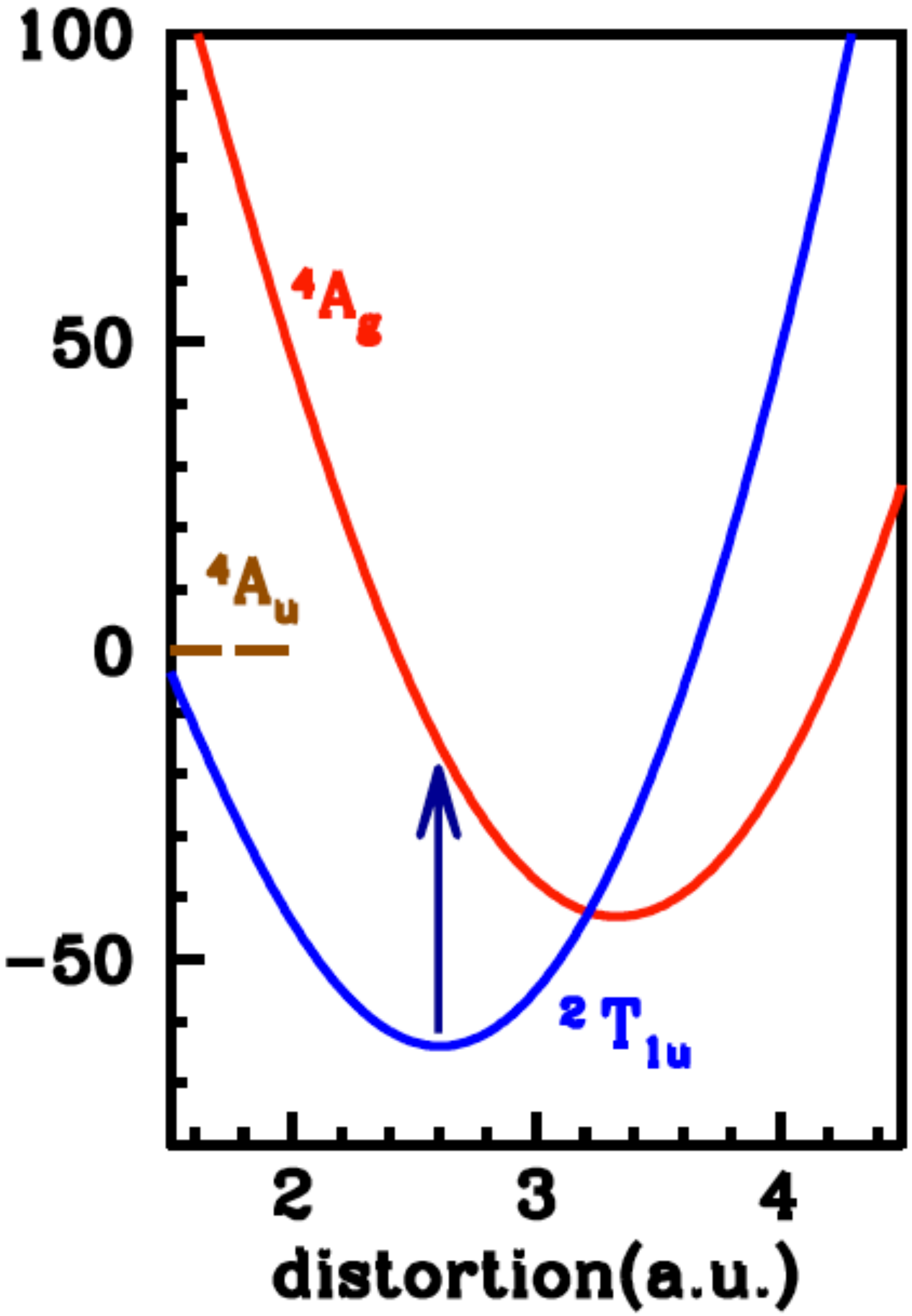
anti-adiabatic approximation



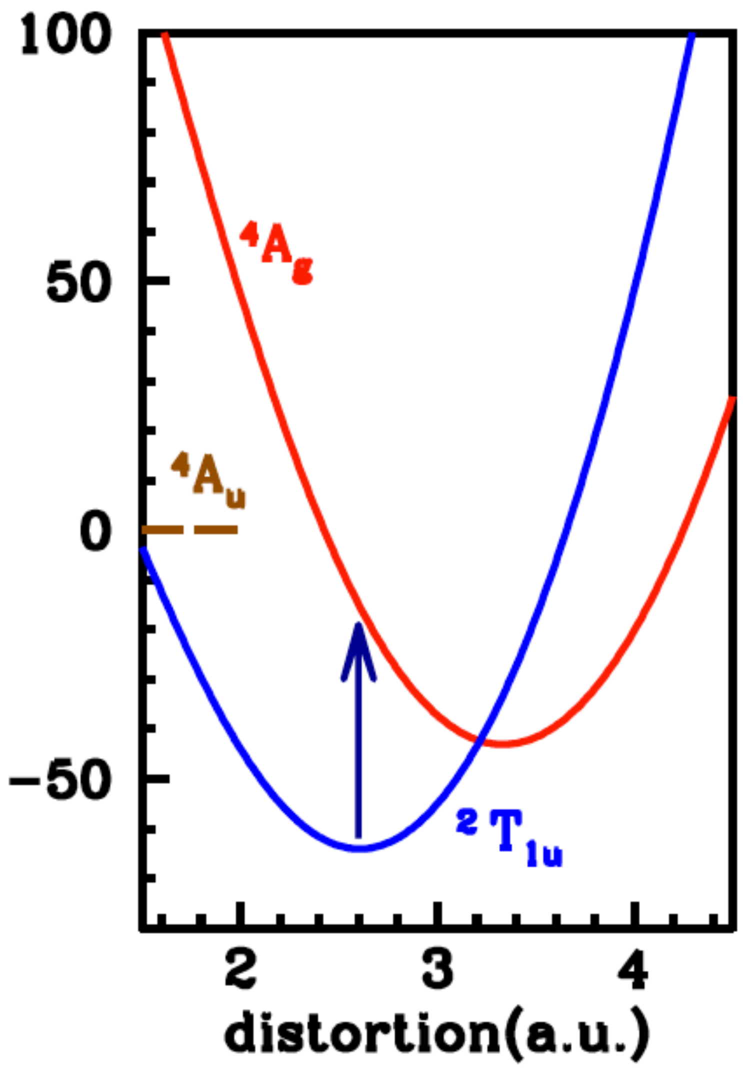

for realist values of $E_{JT}$ the molecular spectrum in the presence of JT effect comprises a low-spin S=1/2 $^2T_{1u}$ ground state and close by a high-spin S=3/2 $^4A_g$ excited state with opposite parity

realistic value

# variational calculation of the full quantum problem




despite its high spin S=3/2 the $^4A_g$ low-lying excited state has a JT distortion stronger than the molecular ground state, and different from the latter, unimodal w.r.t. bimodal

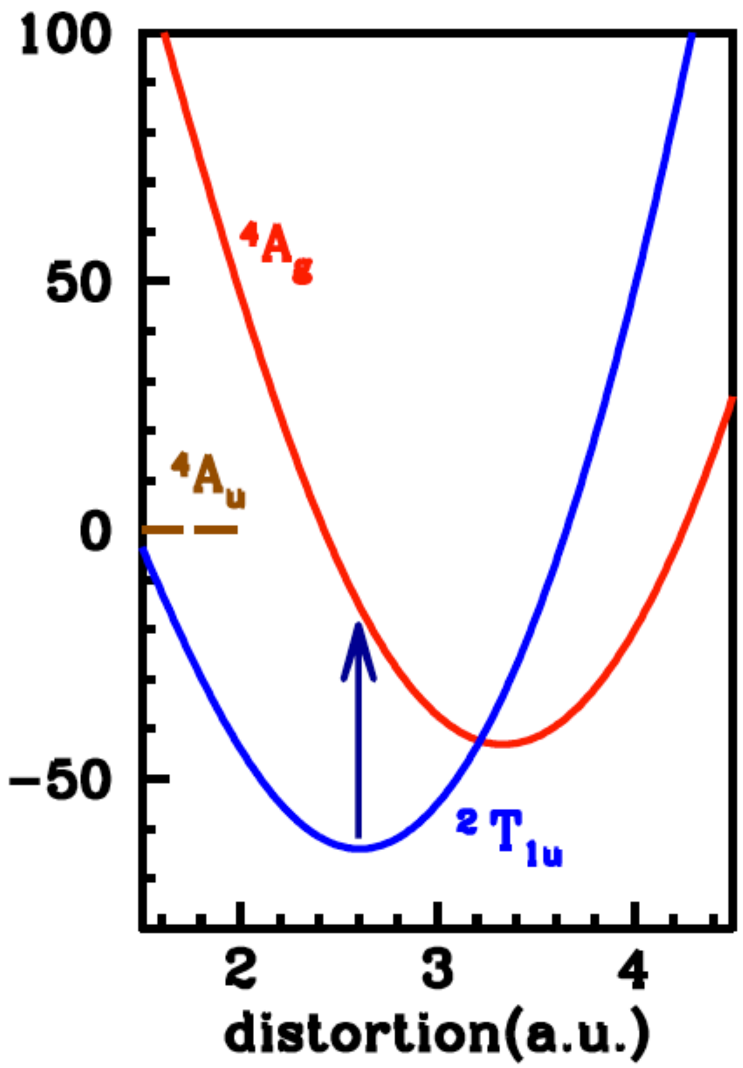



it is very tempting to assume that the $^4A_g$ molecular state turns into a genuine spin-triplet exciton in $A_3C_{60}$, with a huge binding energy $\Delta E_T \sim 1eV$

- the dipole-dipole $F_1$ Slater integral will be reduced by screening but not as much as $F_0$

**a super-exciton!**

can such exciton explain the mid-IR absorption?

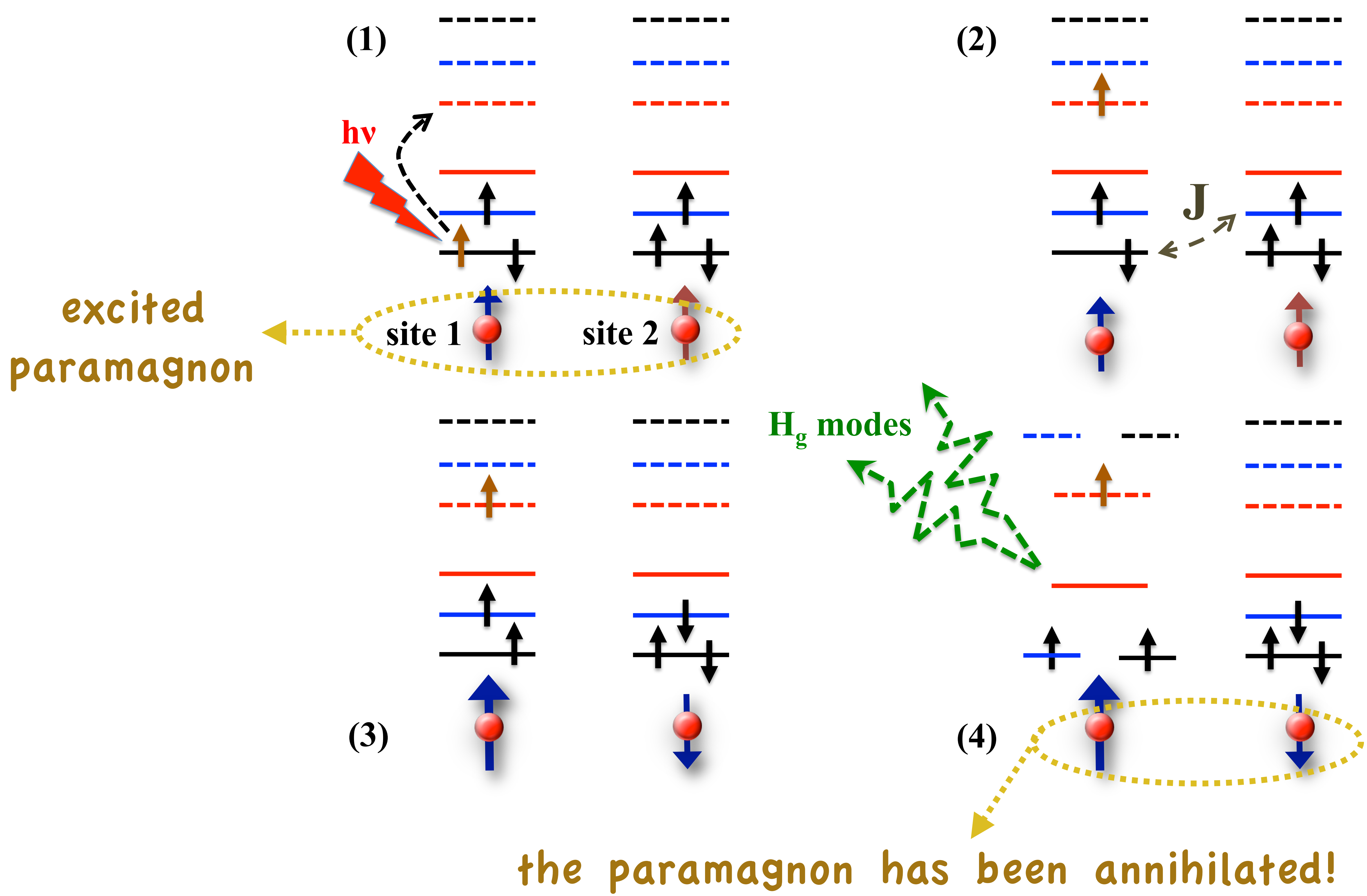



the $^2T_{1u} \rightarrow {}^4A_g$ odd-parity transition has the right spatial symmetry but the wrong spin

is it really a problem?

... not really, since $A_3C_{60}$ are close to becoming AF insulators the excess spin can be easily reabsorbed by S=1 particle-hole excitations

# light-absorption process with the concurrent absorption of a thermally excited paramagnon:



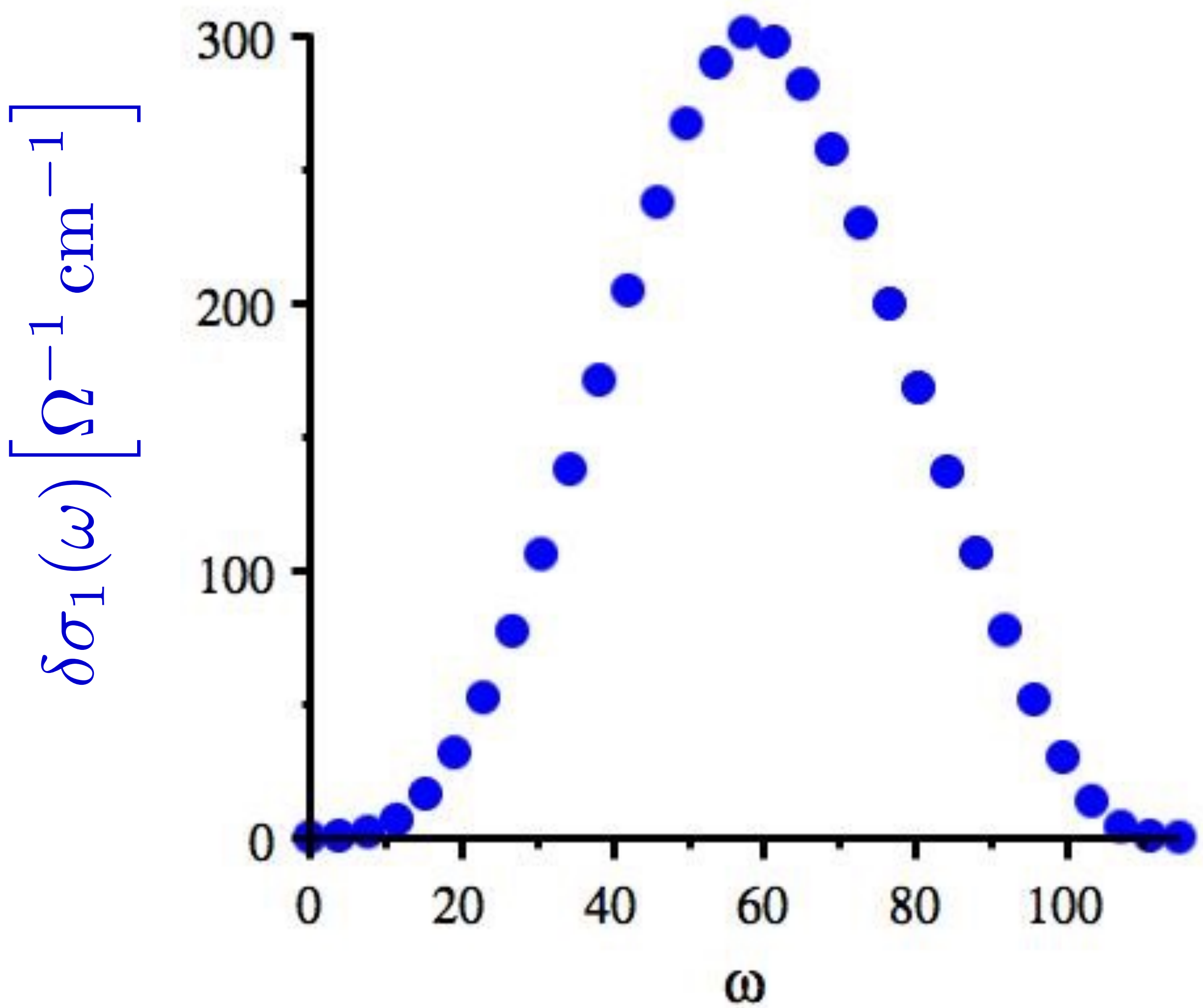
exciton DOS

imaginary part of the dynamical magnetic susceptibility

$$\delta\sigma_1(\omega) \propto \int_0 d\epsilon\, A_{\mathrm{exc}}(\epsilon) \Big[ \theta(\epsilon-\omega)\, b(\epsilon-\omega)\, \chi''(\epsilon-\omega) + \theta(\omega-\epsilon)\, \Big(1 + b(\omega-\epsilon)\Big)\, \chi''(\omega-\epsilon) - b(\epsilon+\omega)\, \chi''(\epsilon+\omega) \Big]$$

Bose distribution

T=25K




- $A_{exc}(\varepsilon)$ narrowly peaked at 30 meV
- $\chi''(\varepsilon)$ that of free quasiparticles with 100 meV bandwidth
- pre-factor fitted by imposing that the peak value is the experimental one, 300 $\Omega^{-1}cm^{-1}$

# change of perspective:

(1) the phenomenon is due to the excitation responsible of the mysterious MIR absorption peak observed in equilibrium at 55 meV

(2) the laser pulse transiently cools down quasiparticles, eventually below the equilibrium $T_c$

# assumptions:

- both exciton non-radiative recombination time and vibration decay time $\geq$ few ps: no heating effect during the 300 fs pulse duration
- strong quasiparticle-quasiparticle collision rate able to establish local equilibrium

in the 300 fs time of the pulse duration

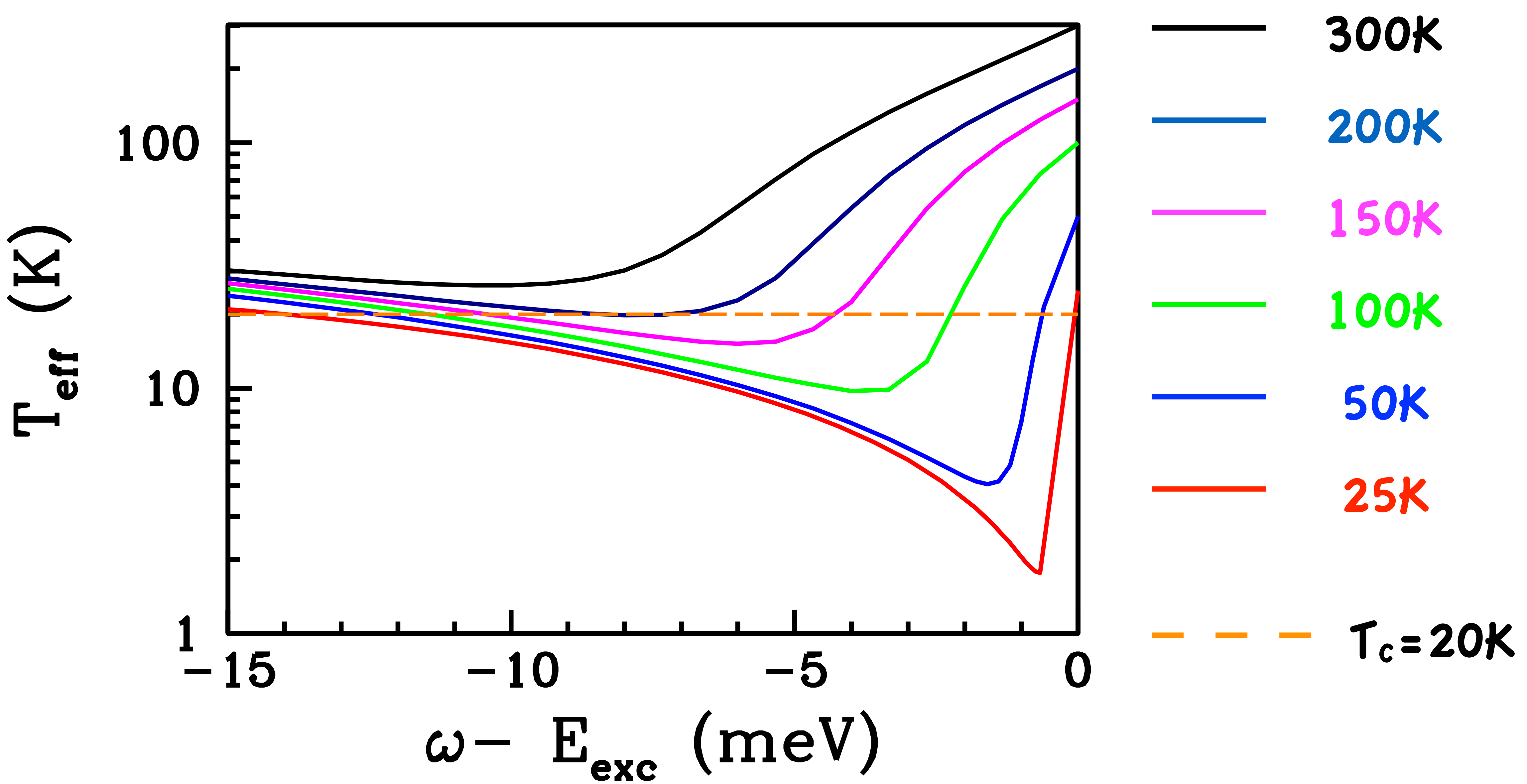
$$T\,\delta S_{\text{quasiparticles}} = \delta Q_{\text{quasiparticles}}$$

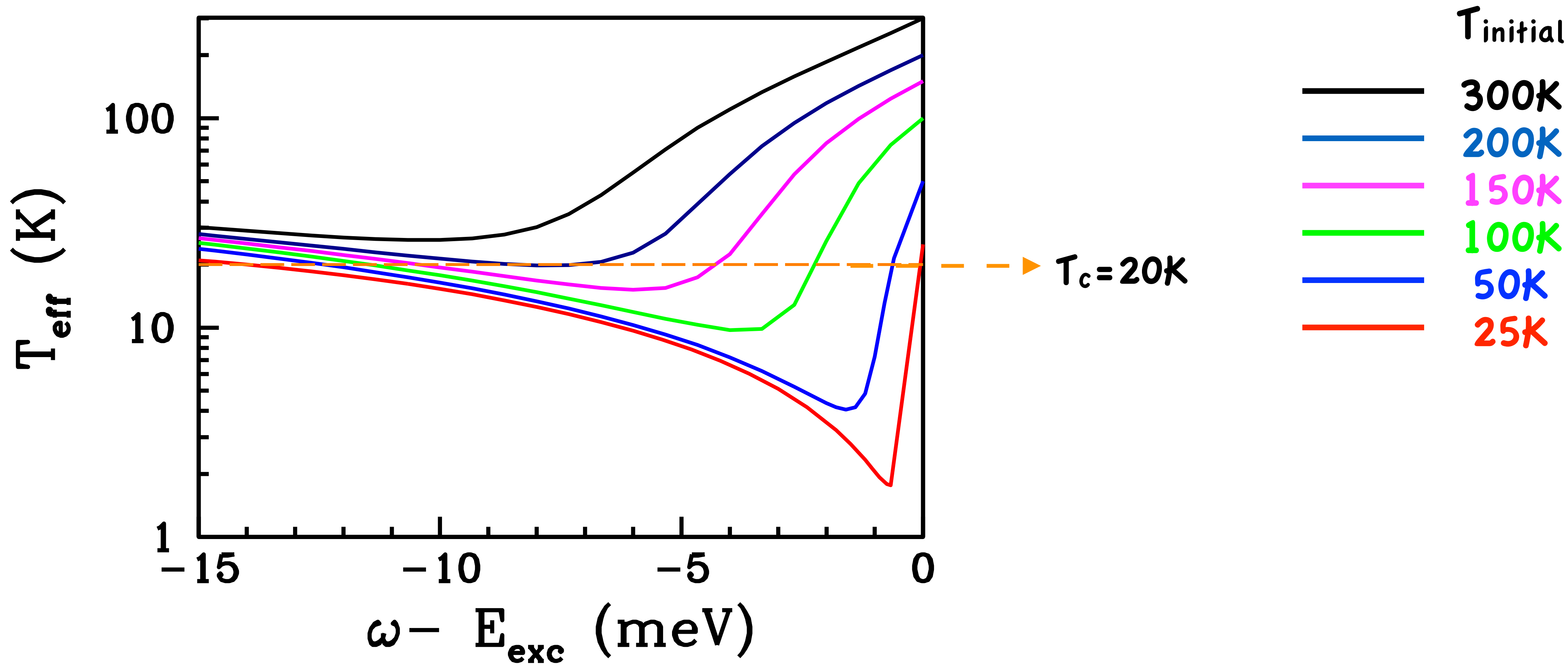
$$T(t)\,\dot{S}_{\text{quasiparticles}}(t) = \Big(\omega - E_{\text{exc}} + \mu(t)\Big)\,\dot{n}_{\text{exc}}\Big(T(t)\Big)$$

exciton energy

light frequency

$T_{eff}$ = T(300 fs)






- $T_{eff}$ after the laser shot can be substantially lower than the external value — thermal S=1 particle-hole excitations being absorbed so that IR pumping can reach the exciton energy

- $T_{eff}$ can be lower than $T_c$ despite the external temperature being higher

# Conclusions

- the molecular spectrum of $C_{60}^{3-}$ shows a strongly-bound odd-parity triplet exciton
- such exciton might be responsible of the anomalous mid-IR response of $A_3C_{60}$
- … and might also provide a simple explanation of the light-induced transient enhancement of $T_c$
- the same mechanism might as well be functioning in other correlated metals on the verge of a Mott transition showing IR absorption peaks attributable to excitons or other long-lived localised excitations that could equally well play the role of entropy sinks.