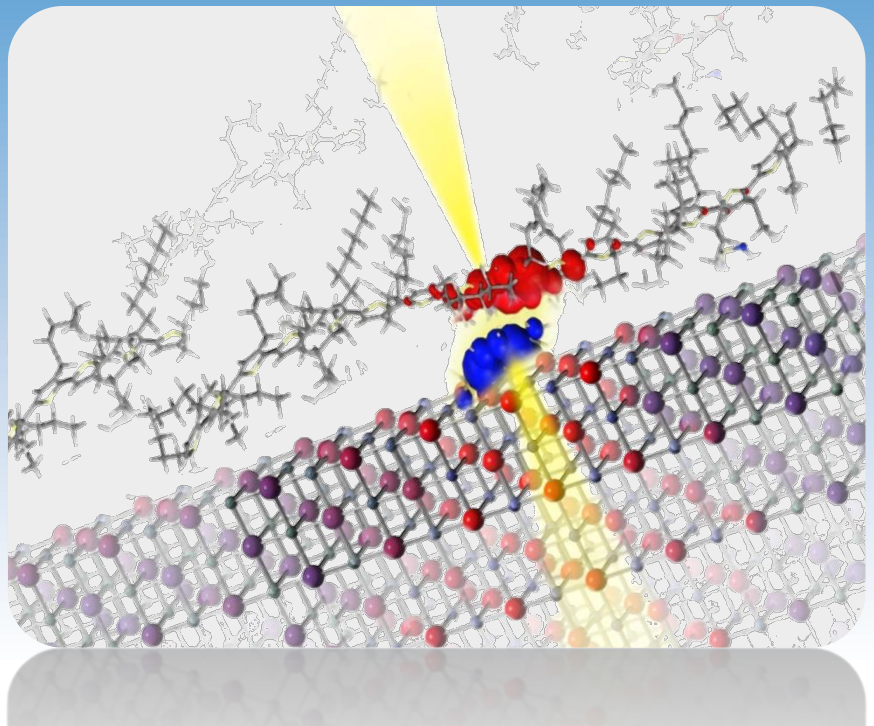
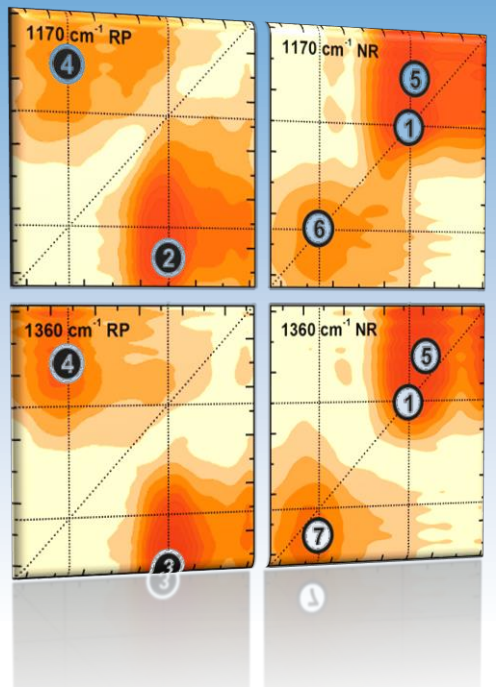
Imperial College London

The Centre for Plastic Electronics

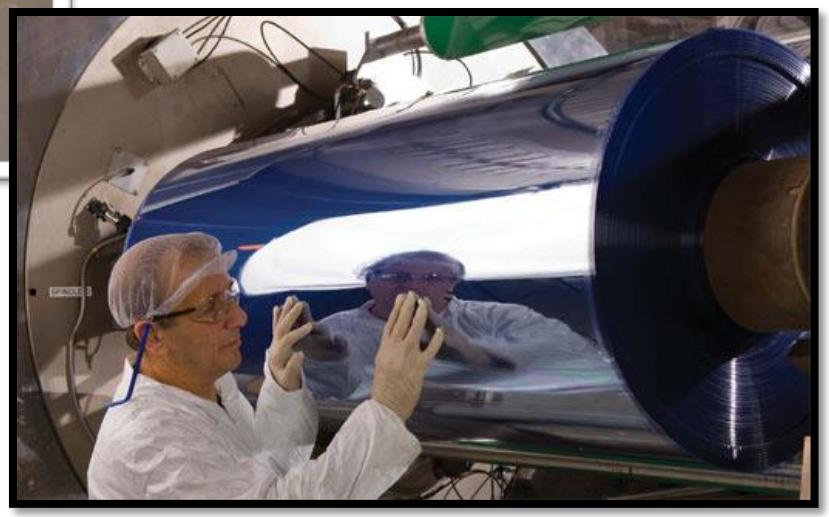
Vibronic phenomena for charge, energy & structural dynamics in organic optoelectronic materials

Artem Bakulin





Organic Electronics



- from solution
- room temperature
- Cheap organic materials
- Roll-to-roll

Organic electronic systems

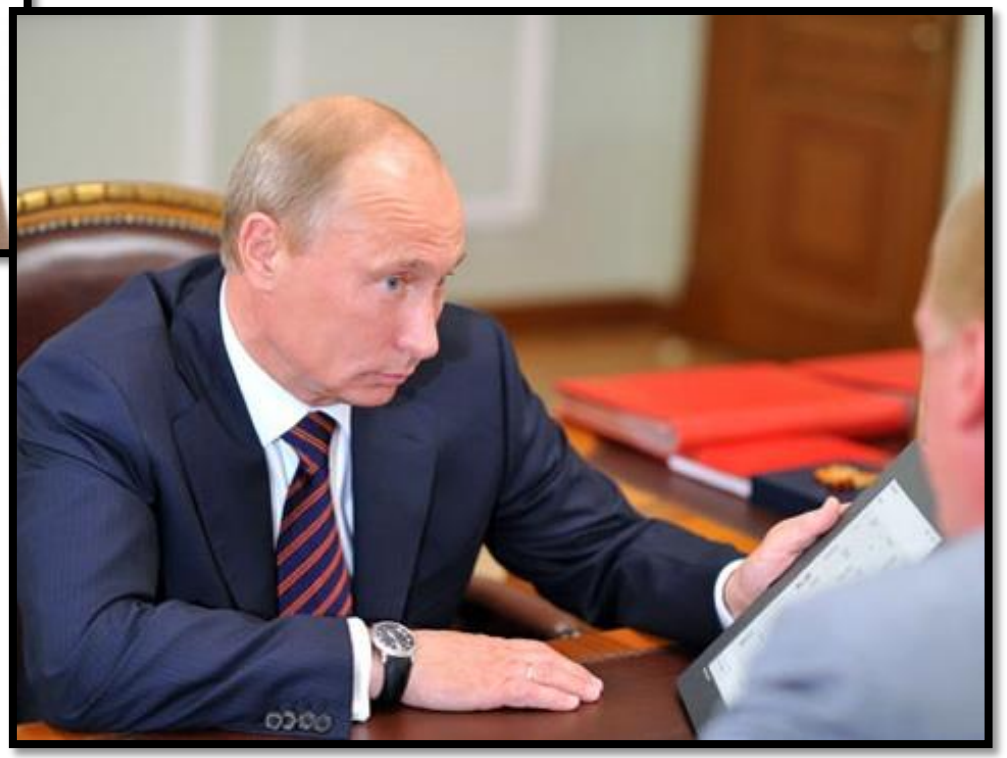
Organic LED Lighting

ANDY ZHOU

Organic Photovoltaics

Eight19

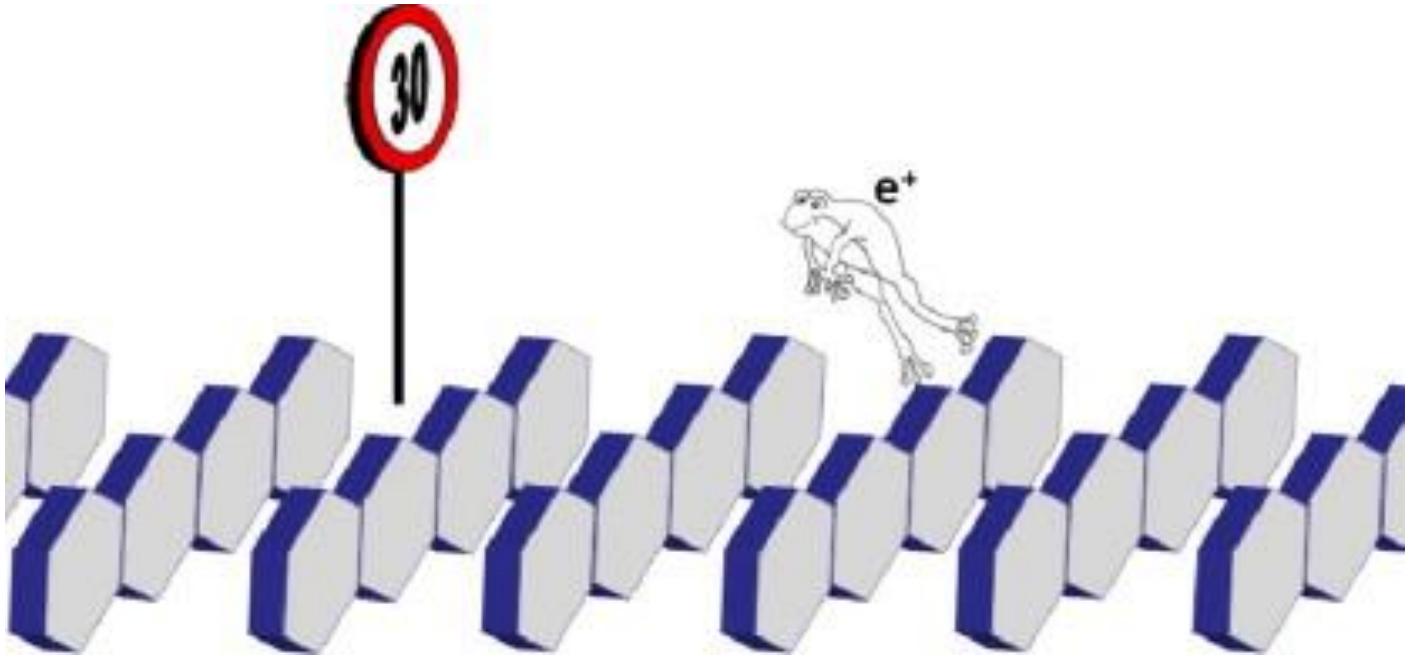
Organic electronic systems



PLASTIC LOGIC

Organic
Field-Effect Transistors

Electron-vibrational coupling in organic materials



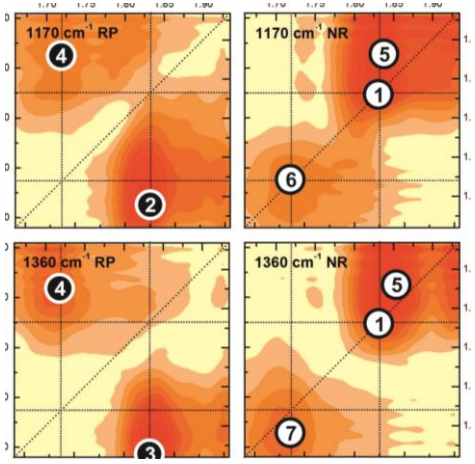
Troisi, *Organic Electronics* (2011)

- 'Soft' material with rich structural dynamics
- Weak electronic couplings
- Charges are localised
- Plenty of local (high-frequency) vibrations

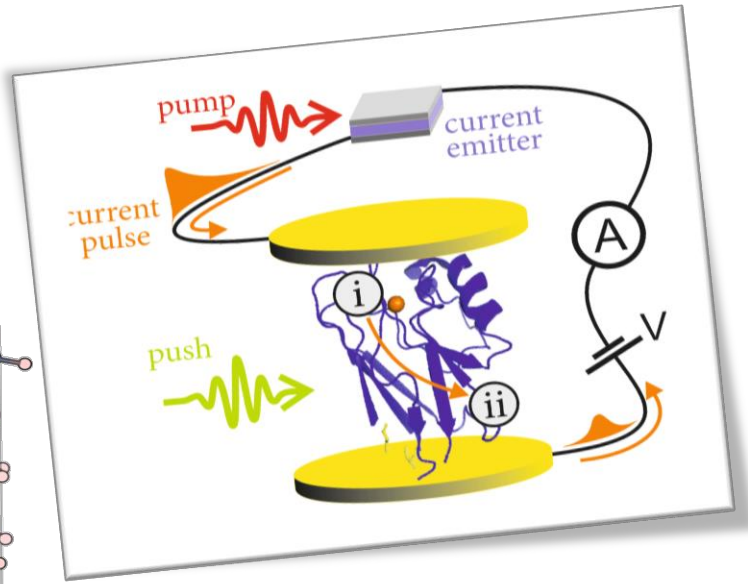
In this talk:

How can vibrational dynamics in organic materials bring new functionalities to optoelectronic systems?

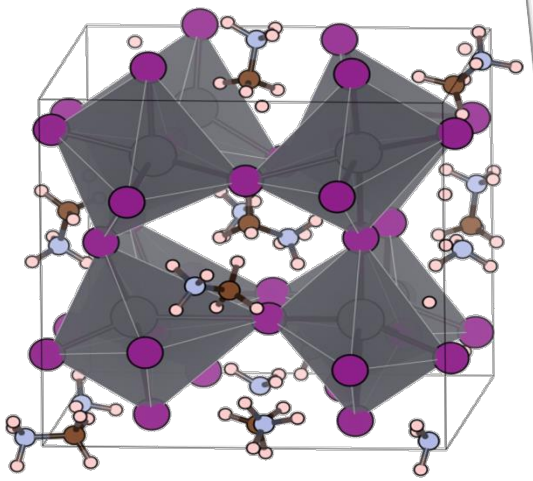
- *Vibronic effects in exciton dynamics (Singlet Fission)*



- *Vibrational control of organic devices*



- *Structural dynamics in perovskites*



Vibronic effects in Singlet Fission

Akshay Rao (Cam)

Dassia Egorova (Kiel)

Andrew Musser (Cam/Sheffield)

Alex Chin (Cam)

Donatas Zigmantas (Lund)

Marcelo Alcocer (Lund)

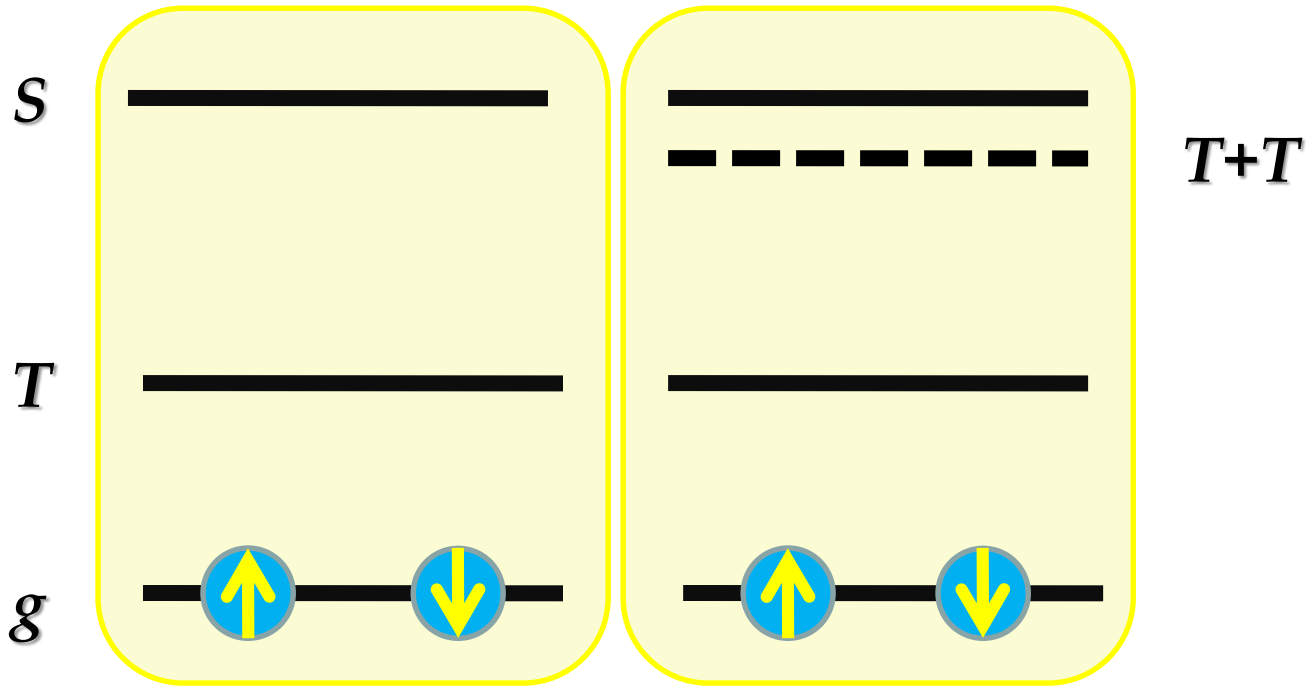
Hannah Stern (Cam)

Sarah Morgan (Cam)

Laserlab Europe

The Integrated Initiative of European Laser Research Infrastructures

Singlet fission (SF) – 2 for 1



- One singlet (S) converts to two triplets (T)
- Process is spin allowed
- Process is energy allowed if 2T<S
- Each triplet may later be used individually

Smith and Michl, *Chem Rev* 2010

Singlet fission (SF) – 2 for 1

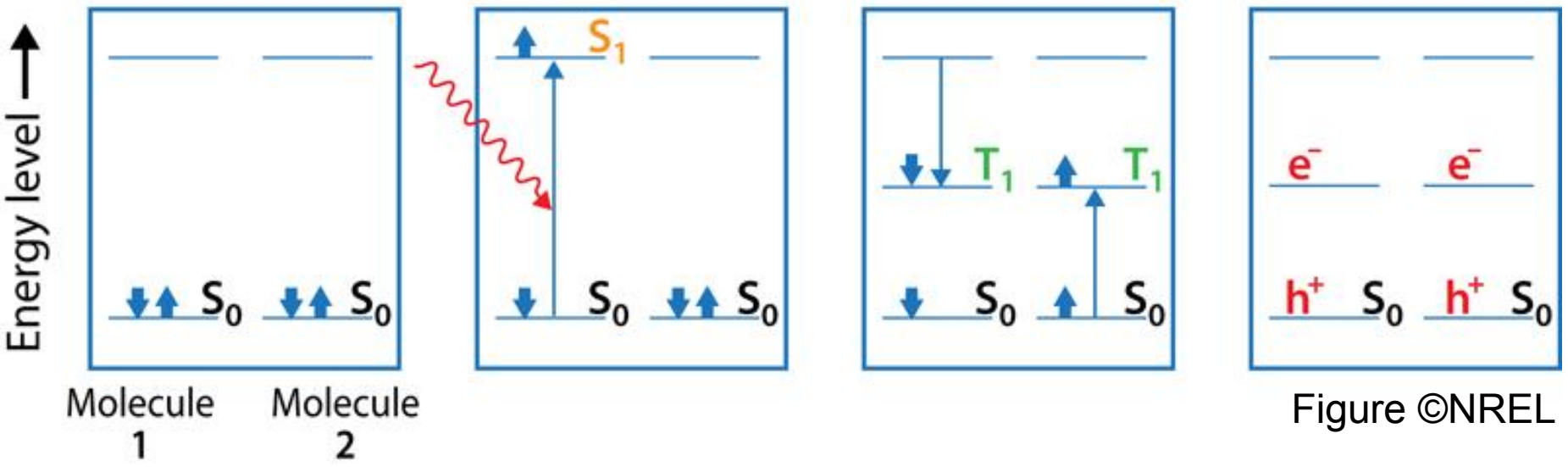
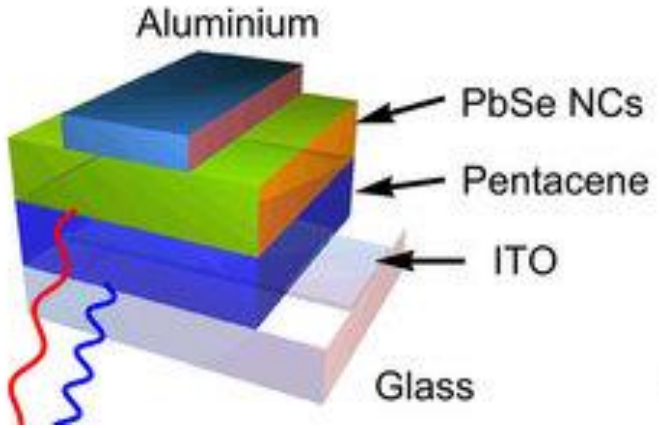


Figure ©NREL

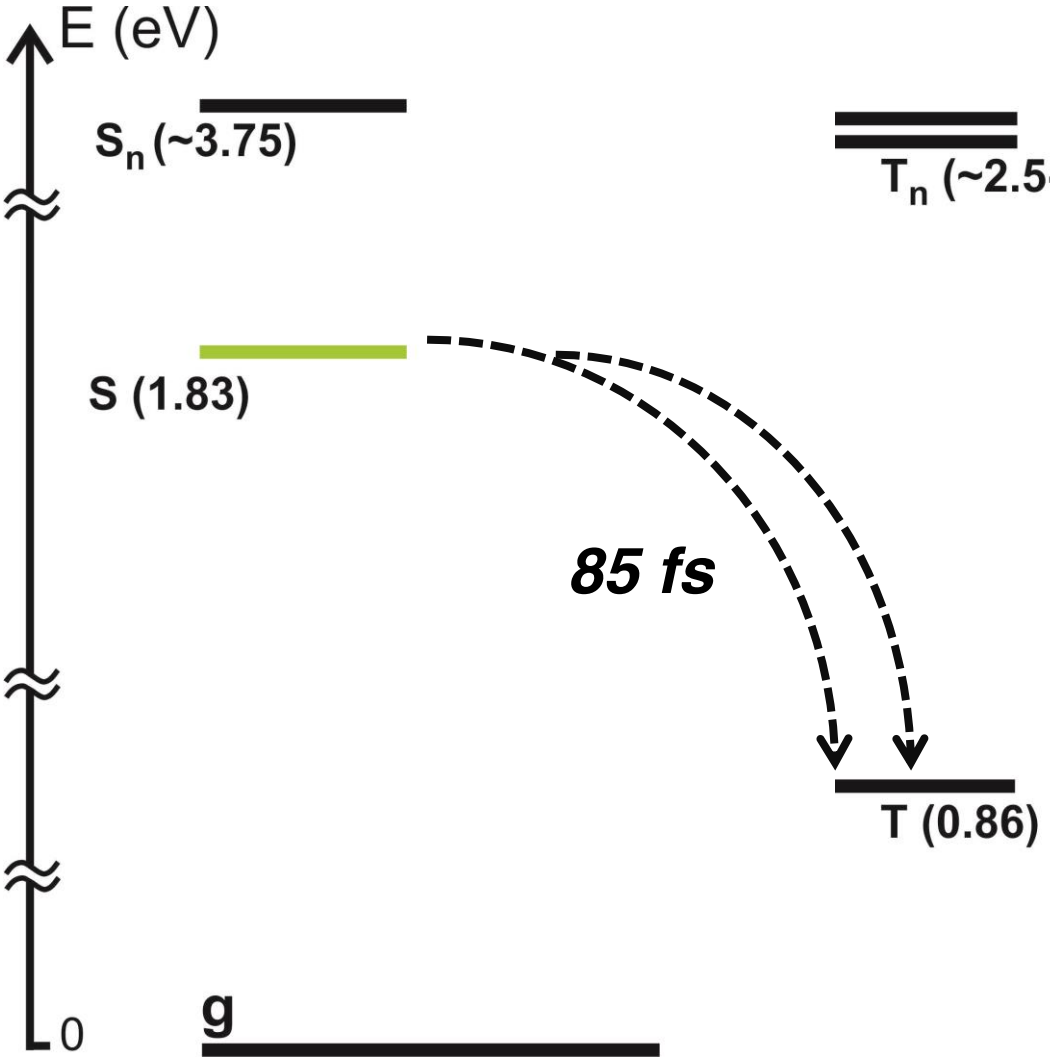


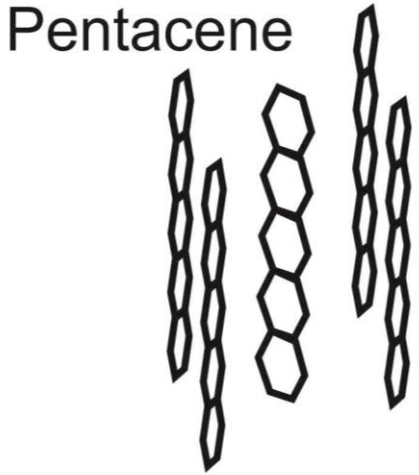
120% EQE solar cell

Wilson et al, Acc. Chem. Res. 2013

Smith and Michl, *Chem Rev* 2010

Fission state diagram for pentacene

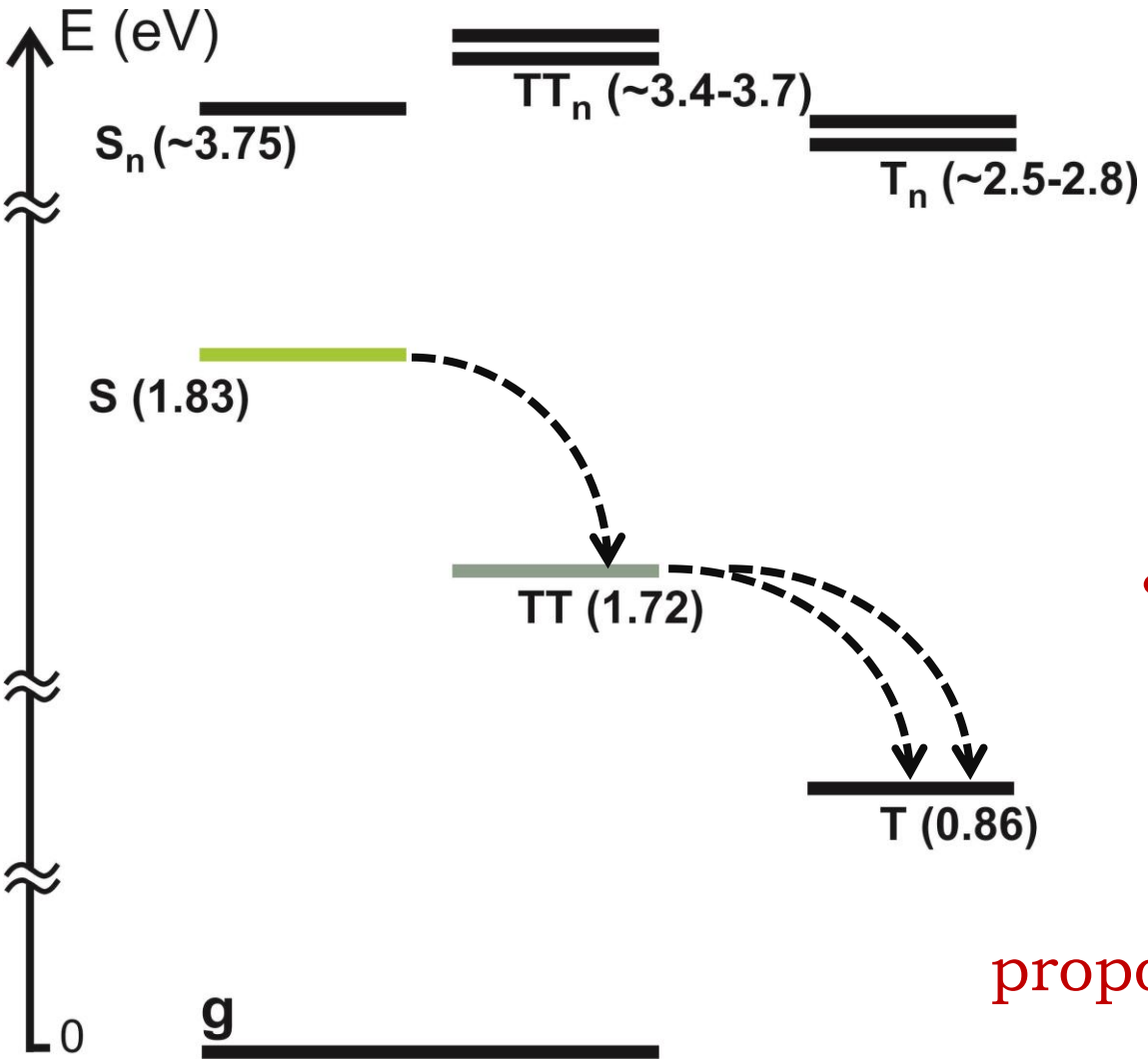


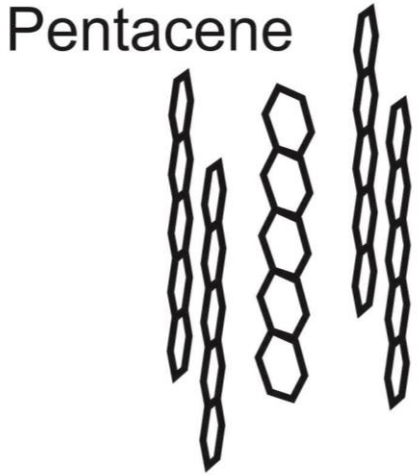


- Driving energy 0.11eV
- 'Fission time' ~85fs

Figure based on Yost et al, *Nat.Chem* 2014
Wilson et al, *JACS*, 2012

Two-step description of fission process

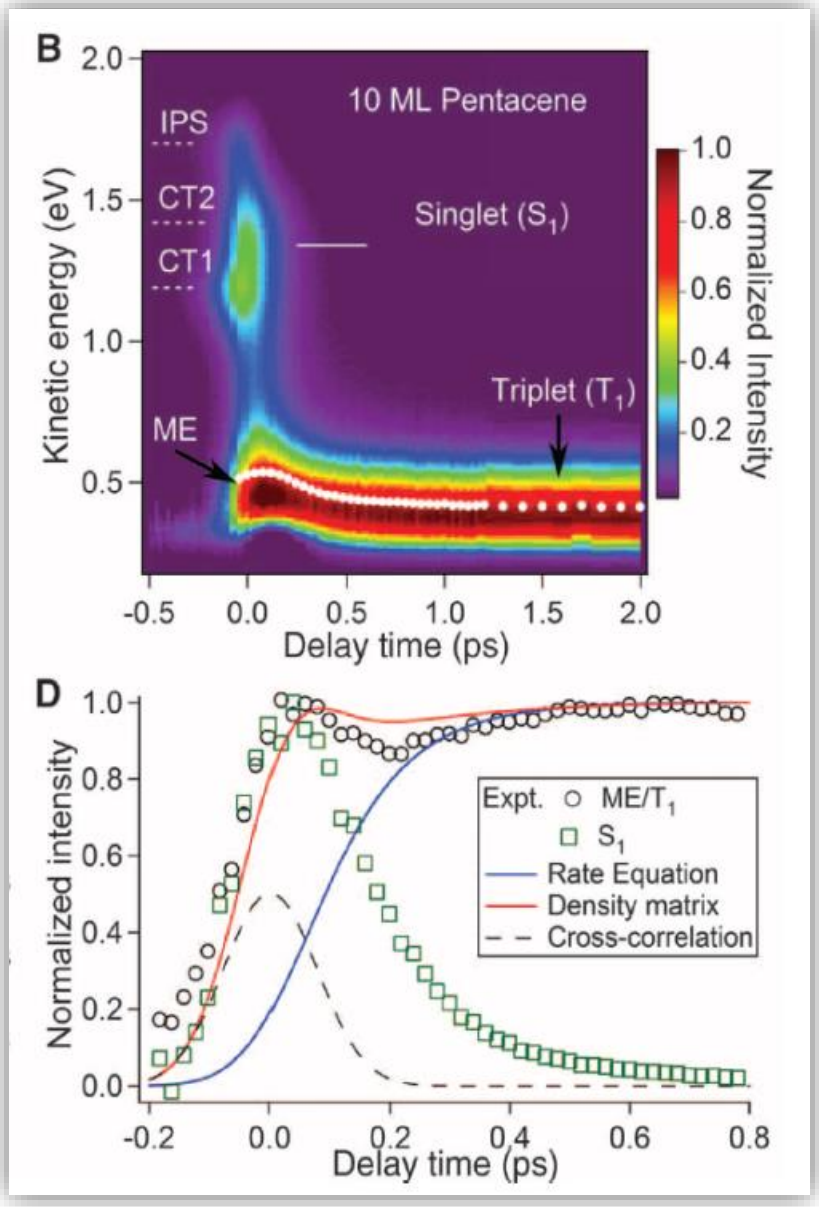


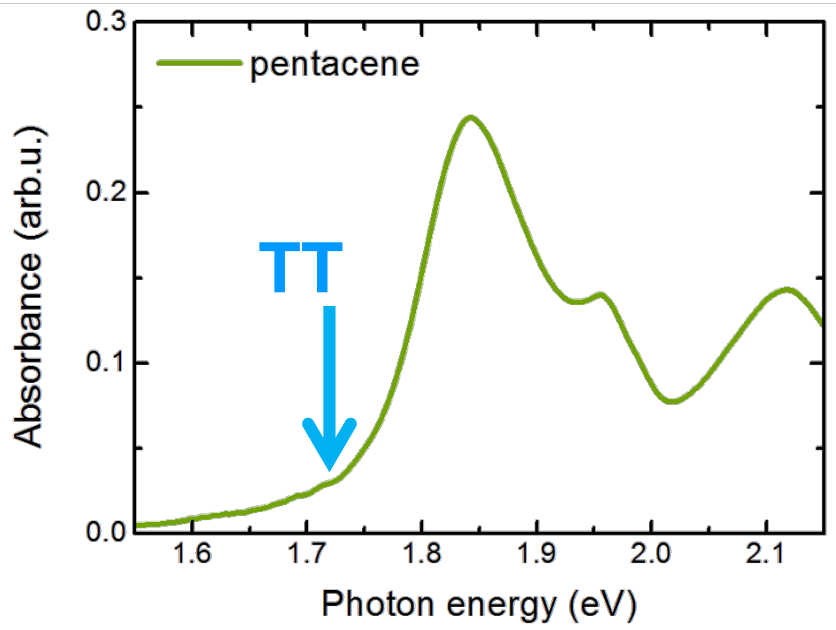


- Driving energy 0.11eV
- 'Fission time' ~85fs
- TT multiexciton is proposed as an intermediate

Figure based on Yost et al, *Nat.Chem* 2014
Wilson et al, *JACS*, 2012

Strong vs Weak coupling



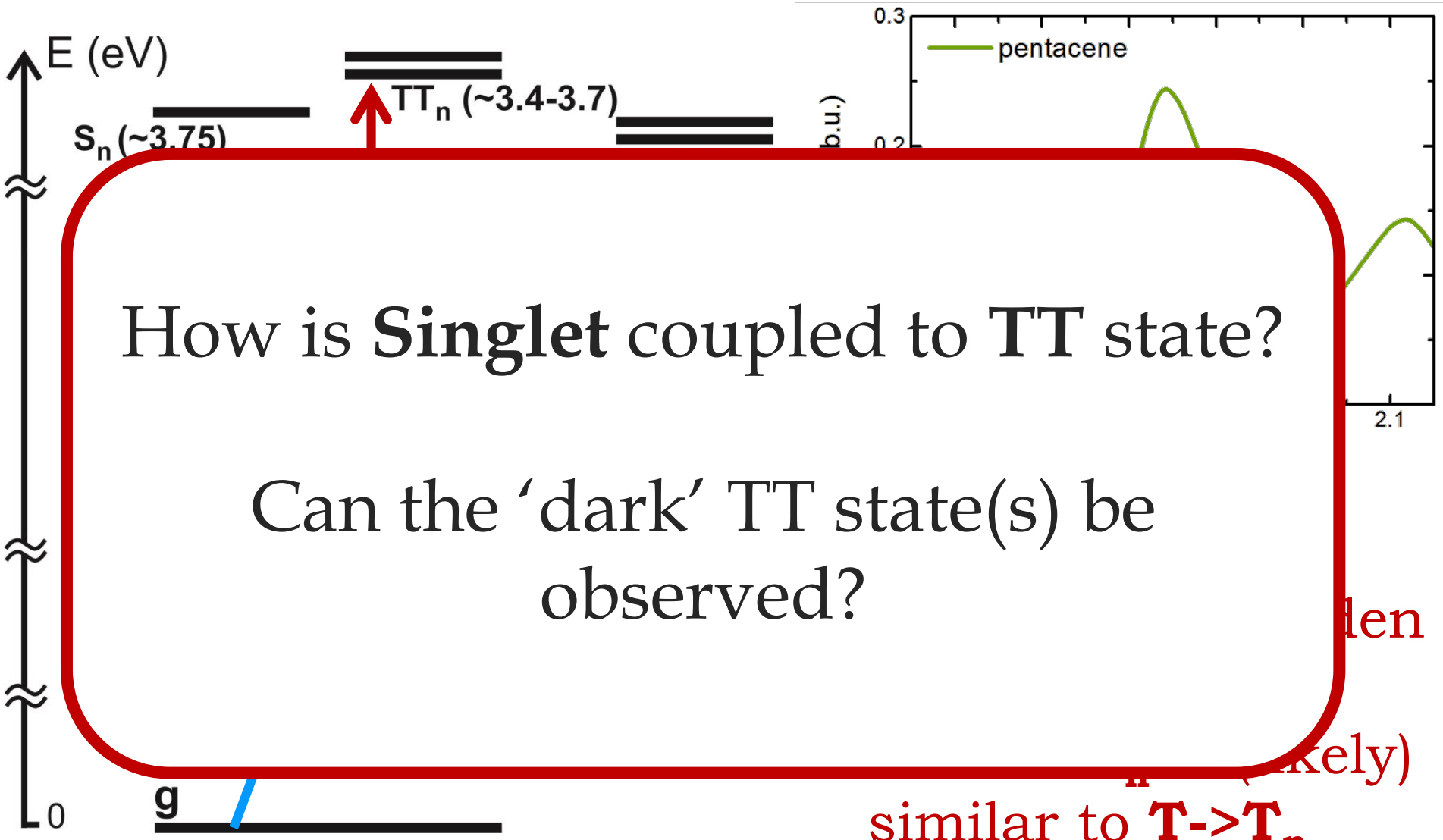


- Fast fission (and PE data) can be explained by strong +1000 cm^{-1} S-TT coupling

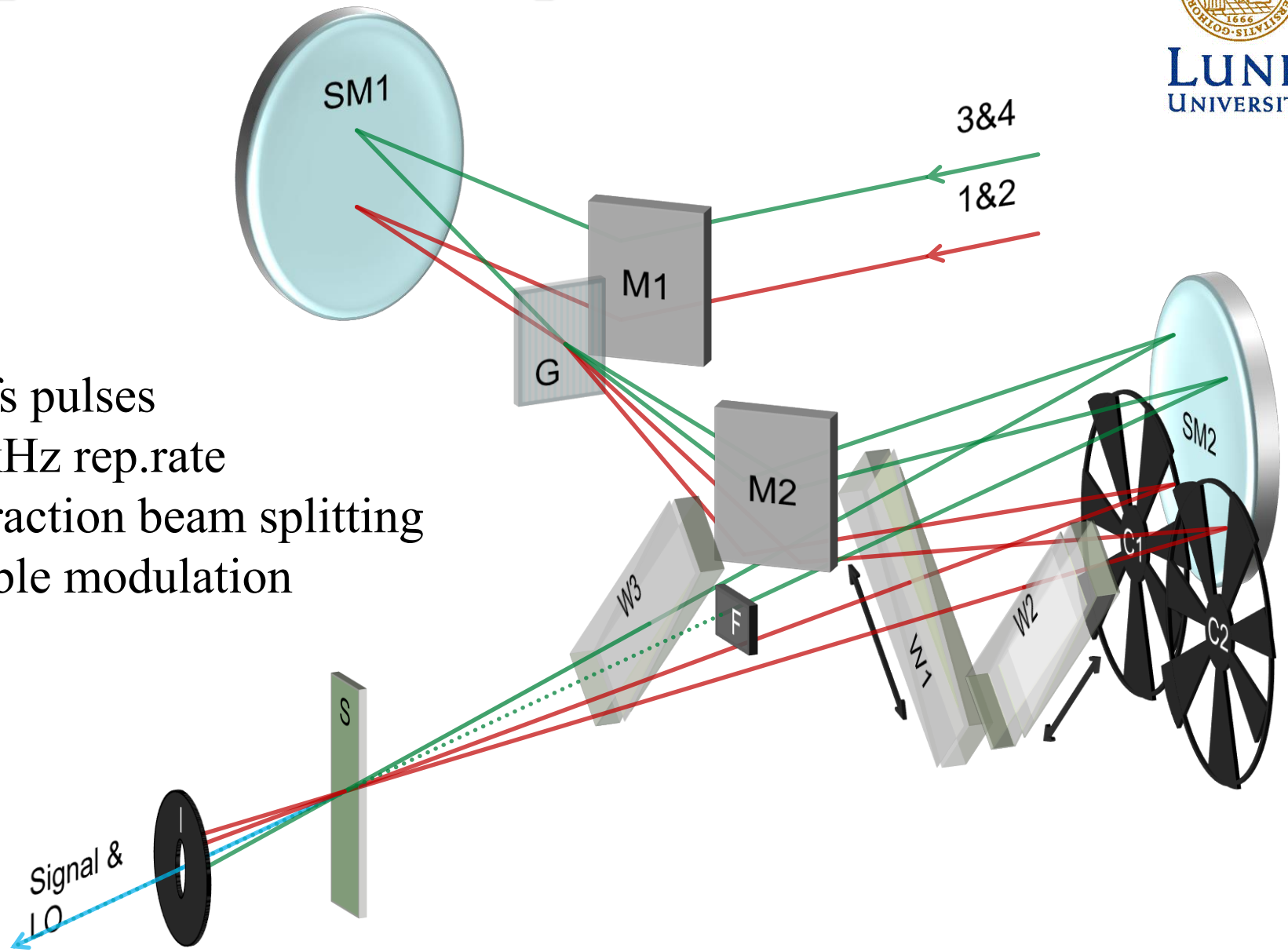
- No evidence of strong coupling in most direct measurements

XY Zhu et al, Sciences (2011)

Spectral signatures of multiexciton TT state



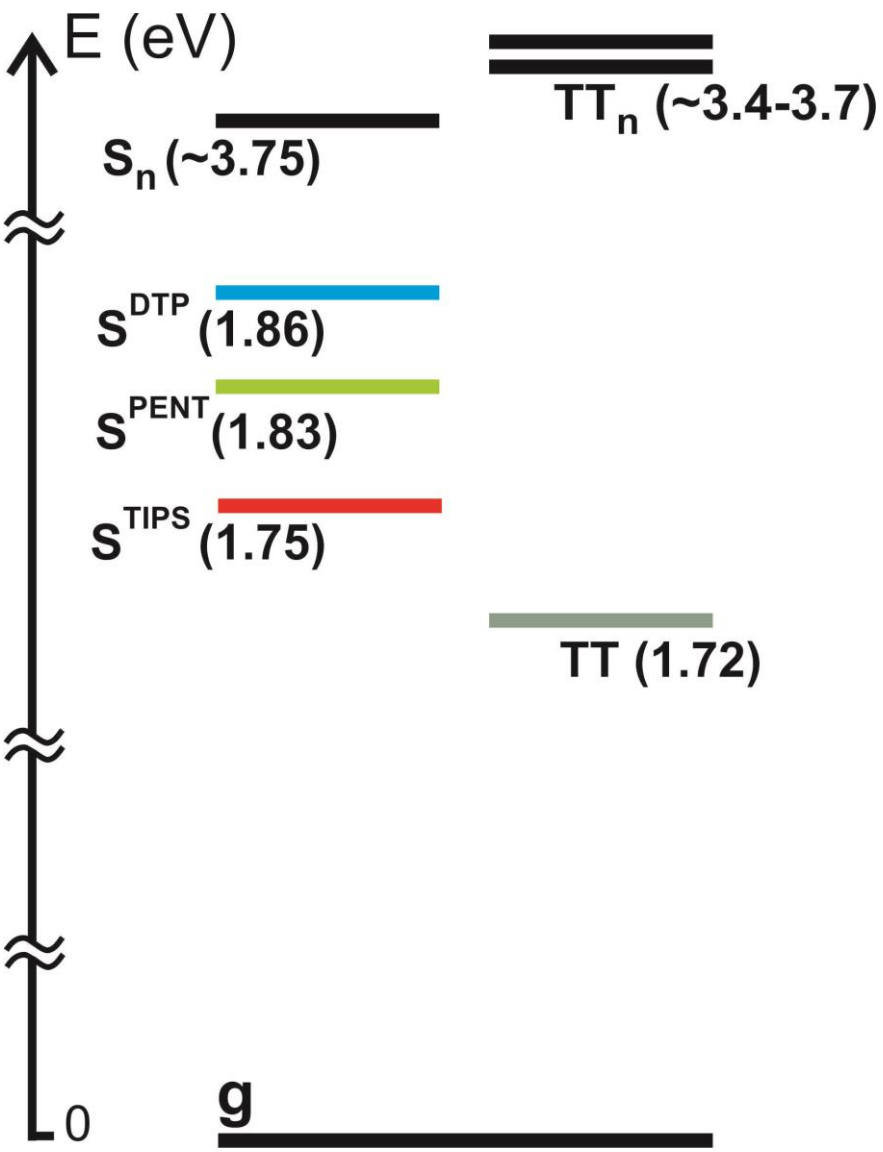
2D photon echo setup

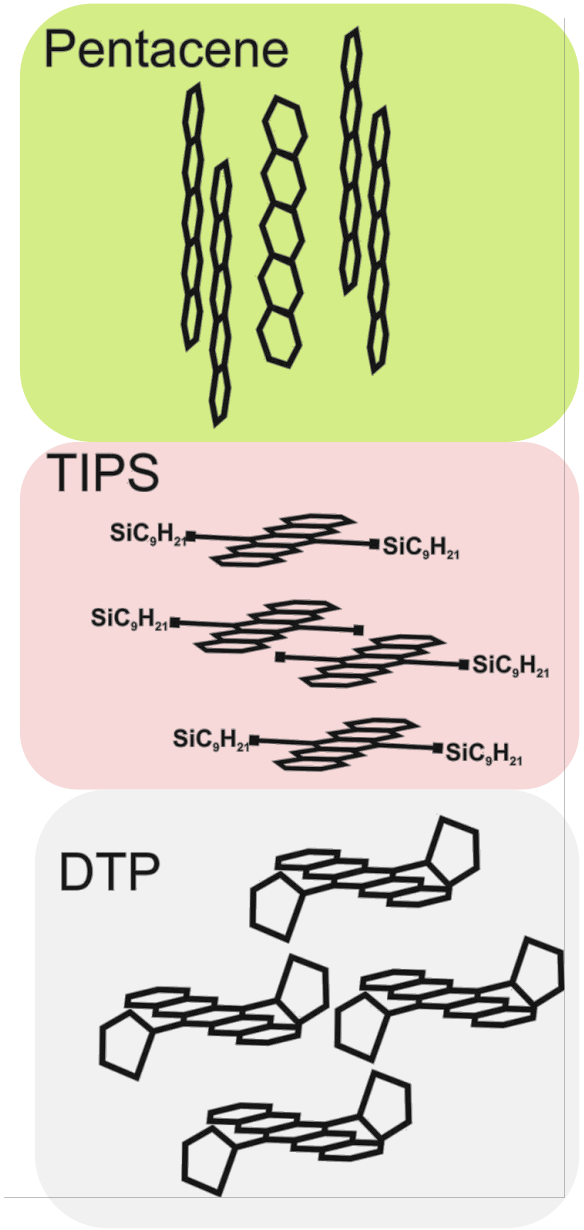


- 13-fs pulses
- 20 kHz rep.rate
- diffraction beam splitting
- double modulation

Brixner et al *JCP* 2004

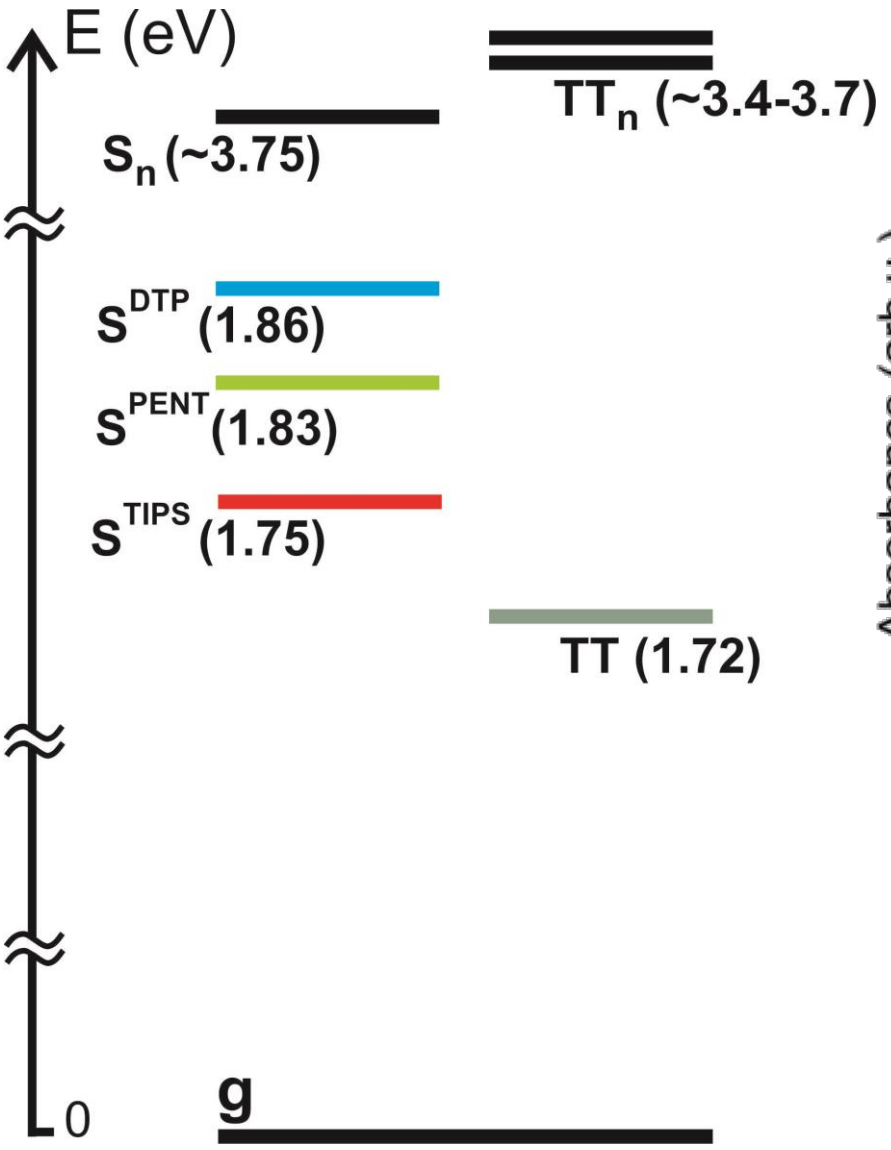
Tuning the driving energy with molecular packing

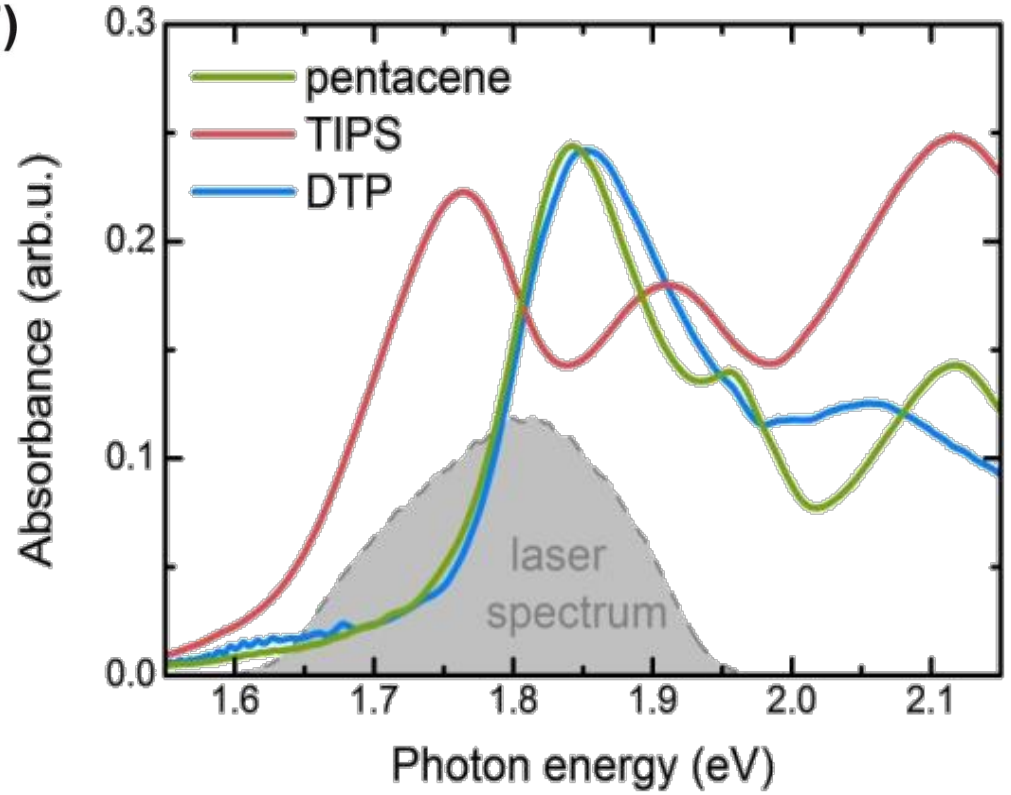




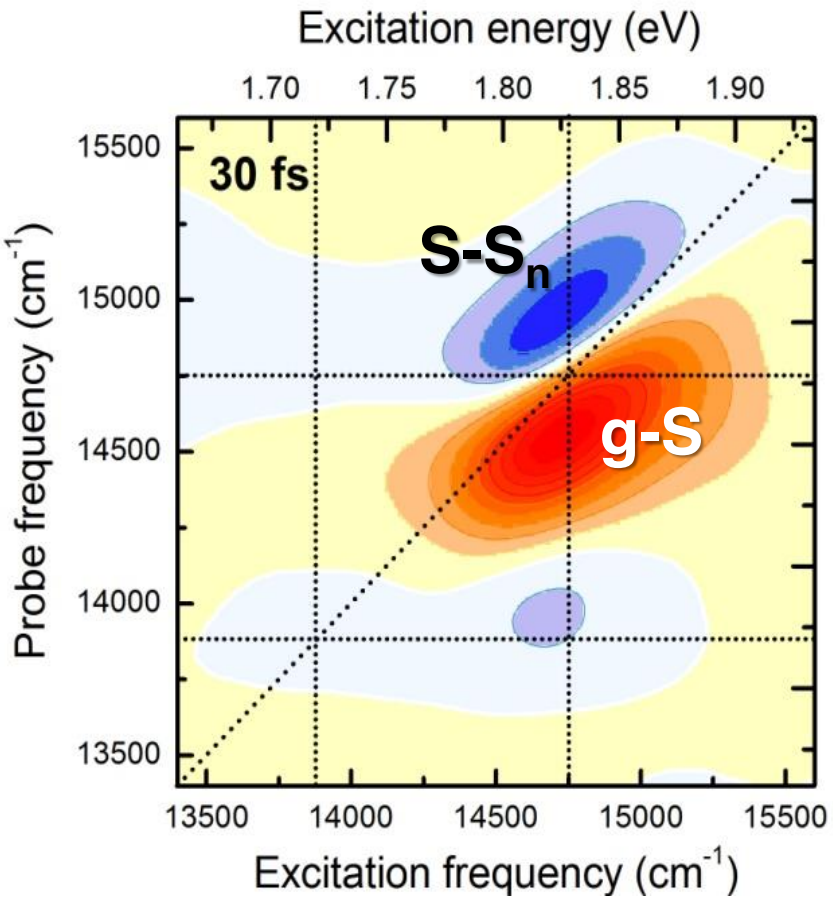
Based on Yost et al, *Nat.Chem* 2014

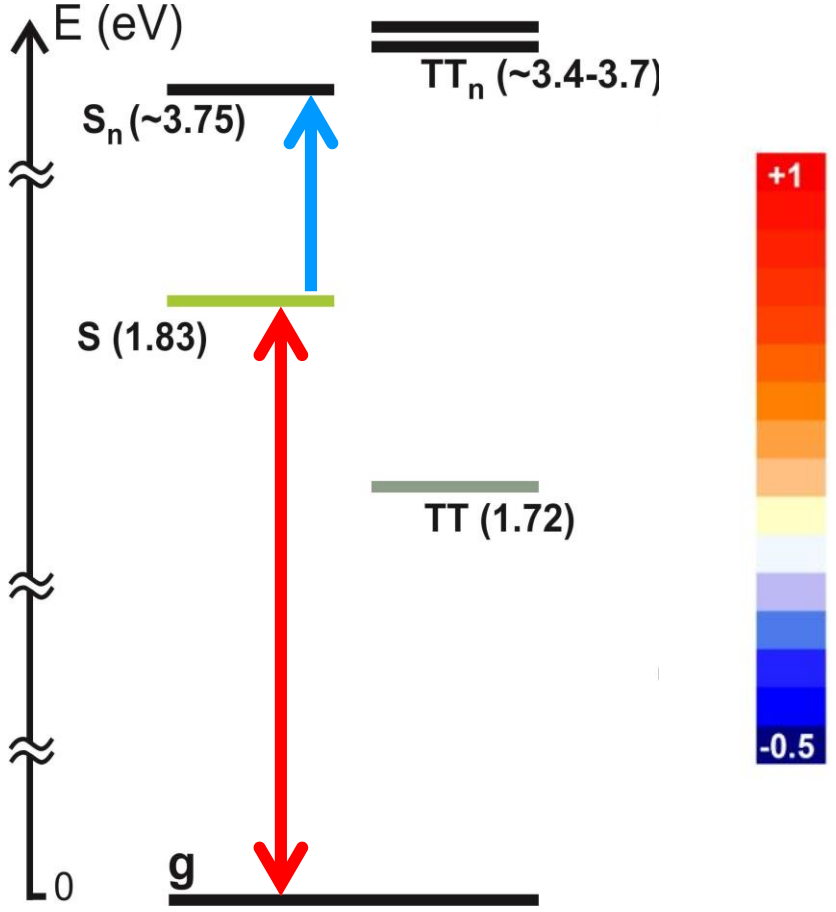
Absorption and laser spectra





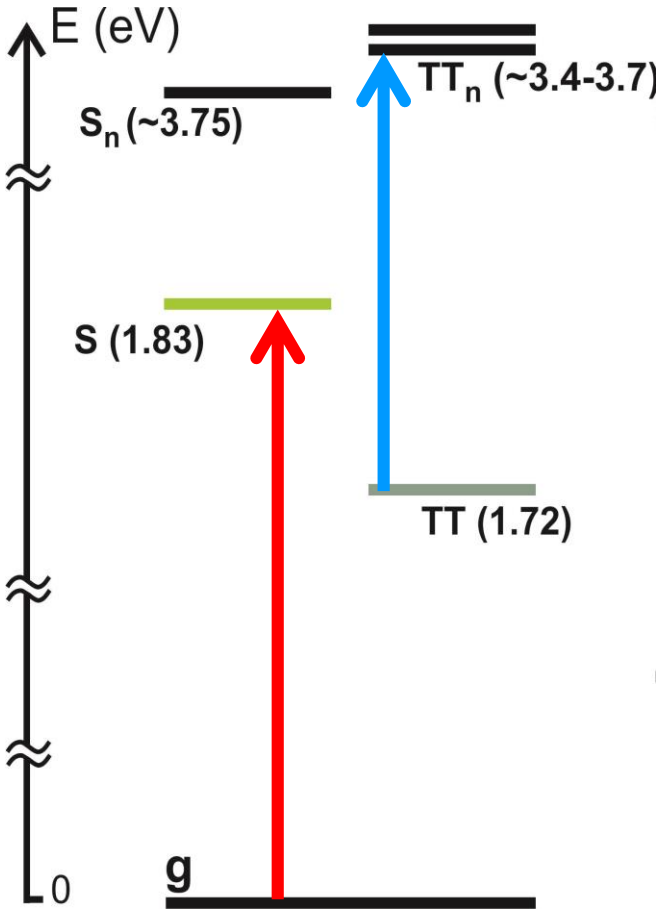
Absorptive 2D spectra

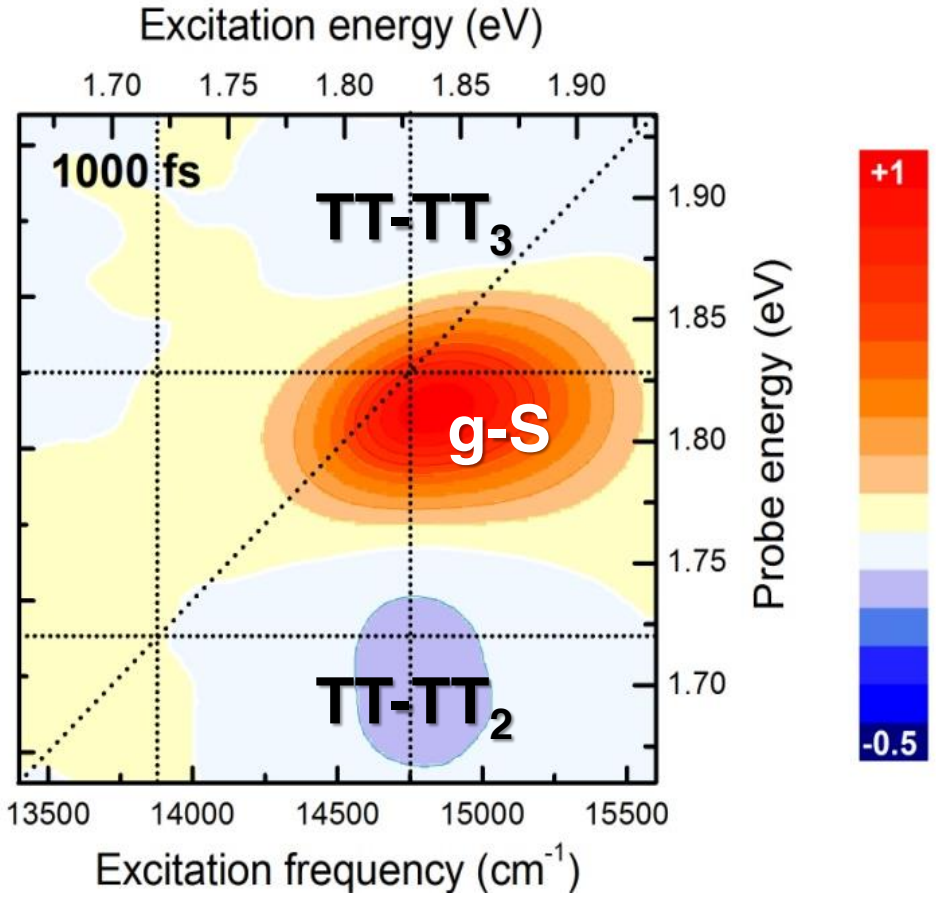




- Short time – Singlet response

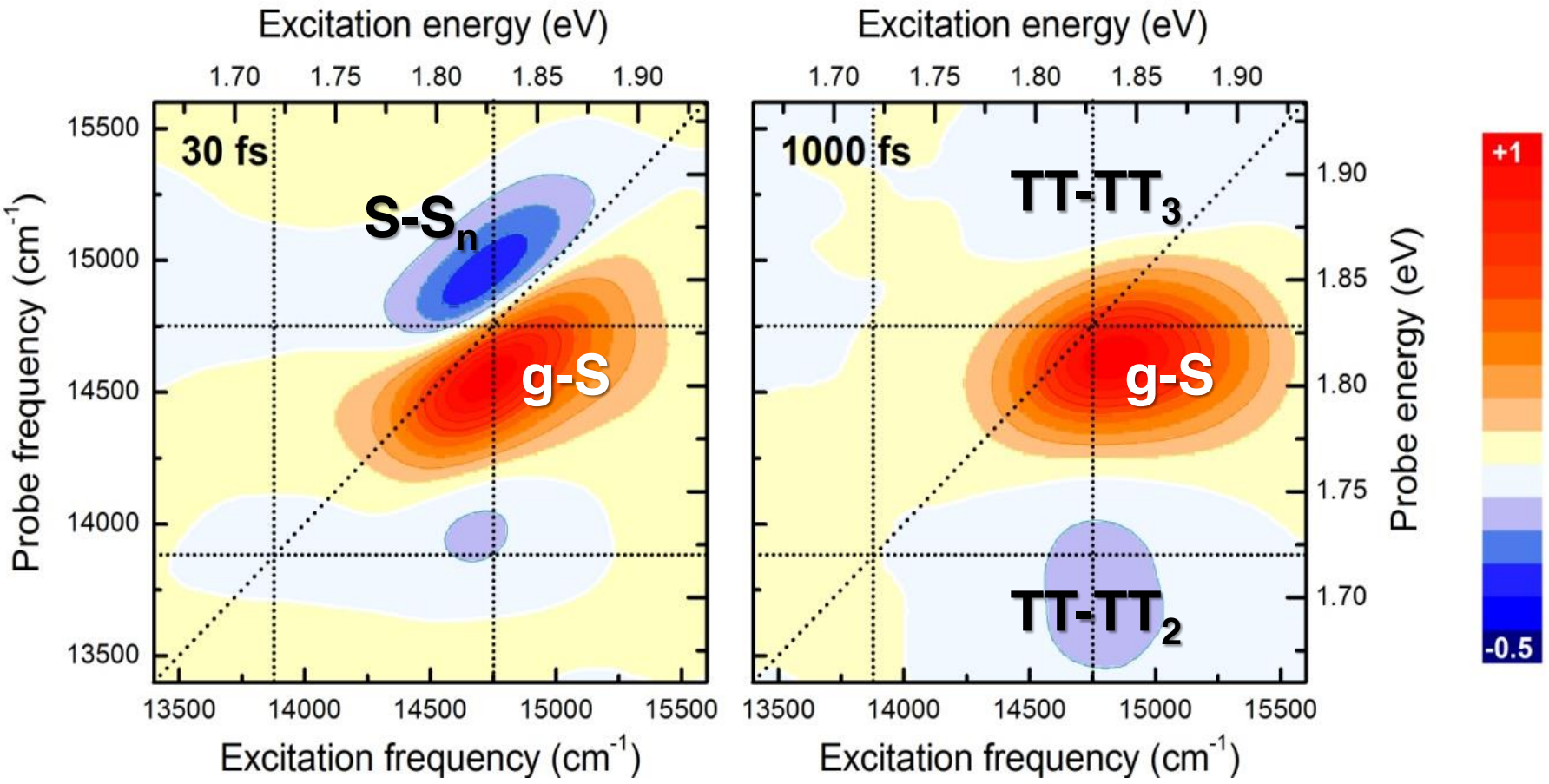
Absorptive 2D spectra





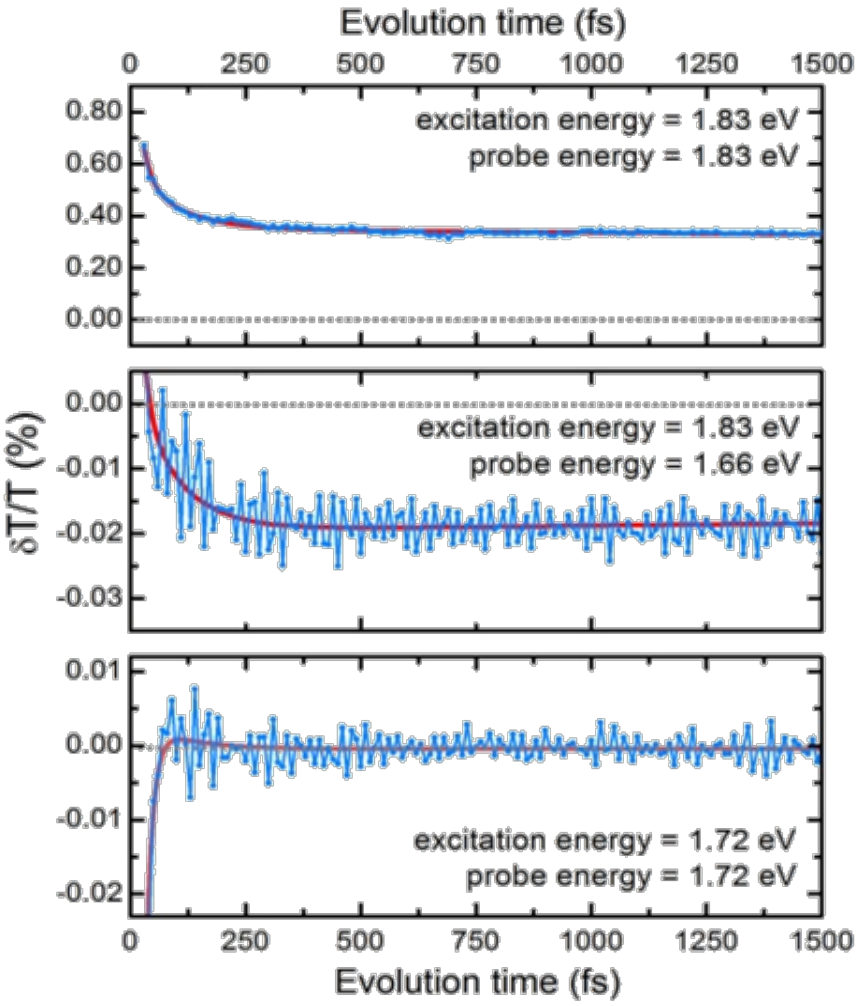
- Short time – Triplet response

Absorptive 2D spectra



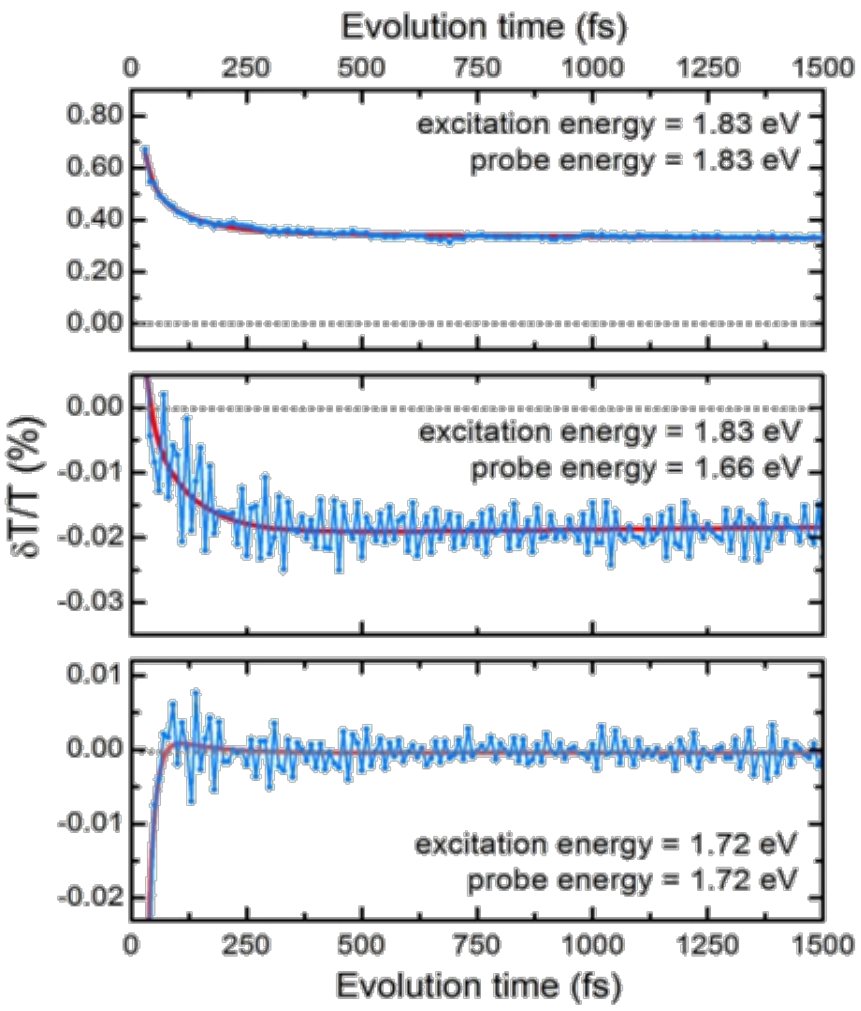
- Singlet and triplet are observed after exciting S
- Fission occures on ~90fs time scale
- No sign of multi-exciton state TT

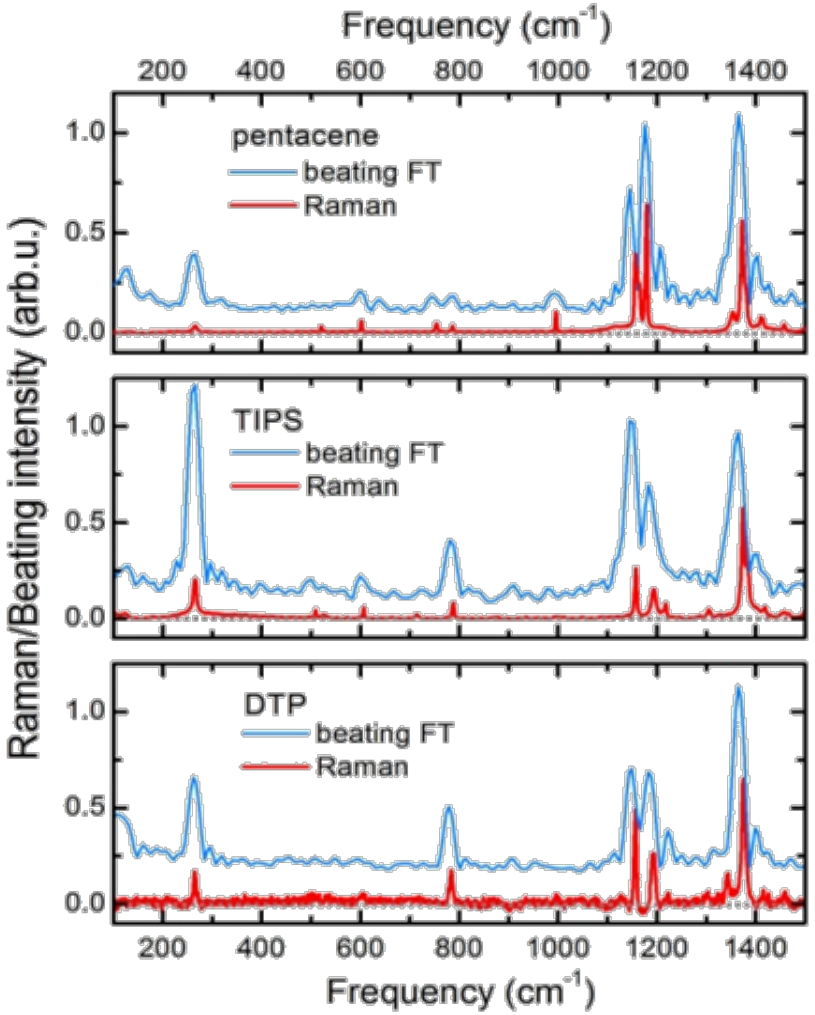
Beatings observed in 2D



- Beatings are clearly seen
- Beatings can have vibrational or electronic nature

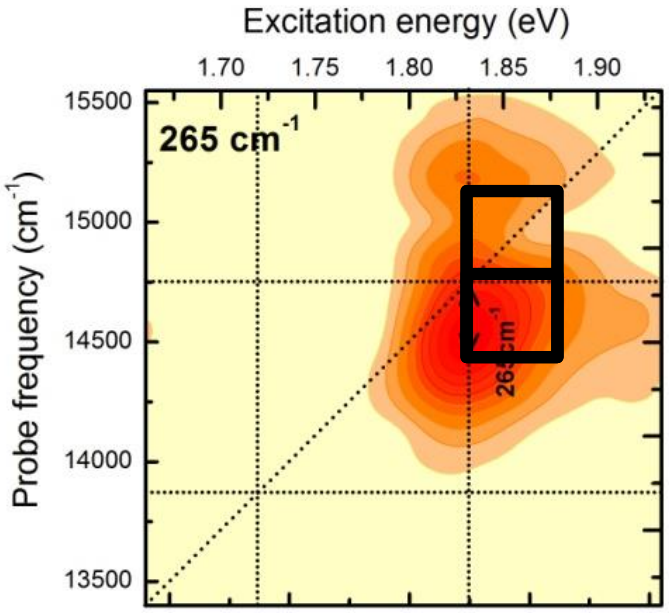
Beatings observed in 2D

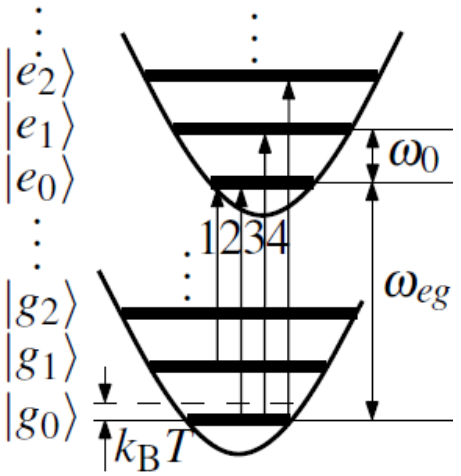


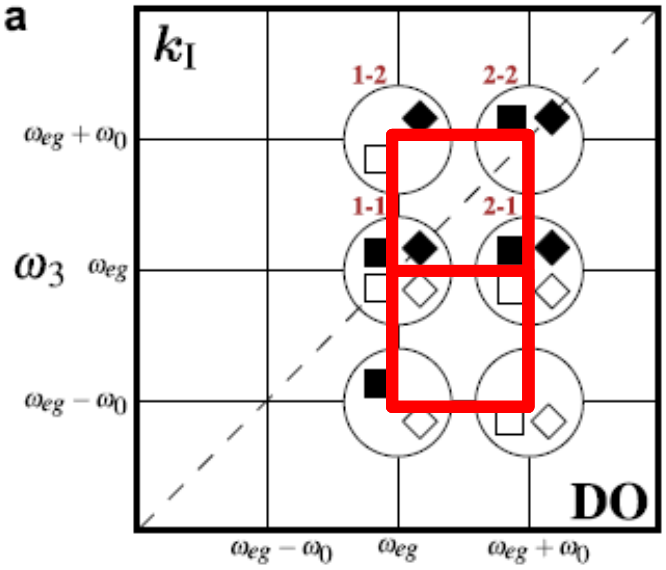


- Beatings are clearly seen
- All the observed beatings are vibronic
- No evidence for (long living) electronic coherence

Beating map for low-energy vibrational modes



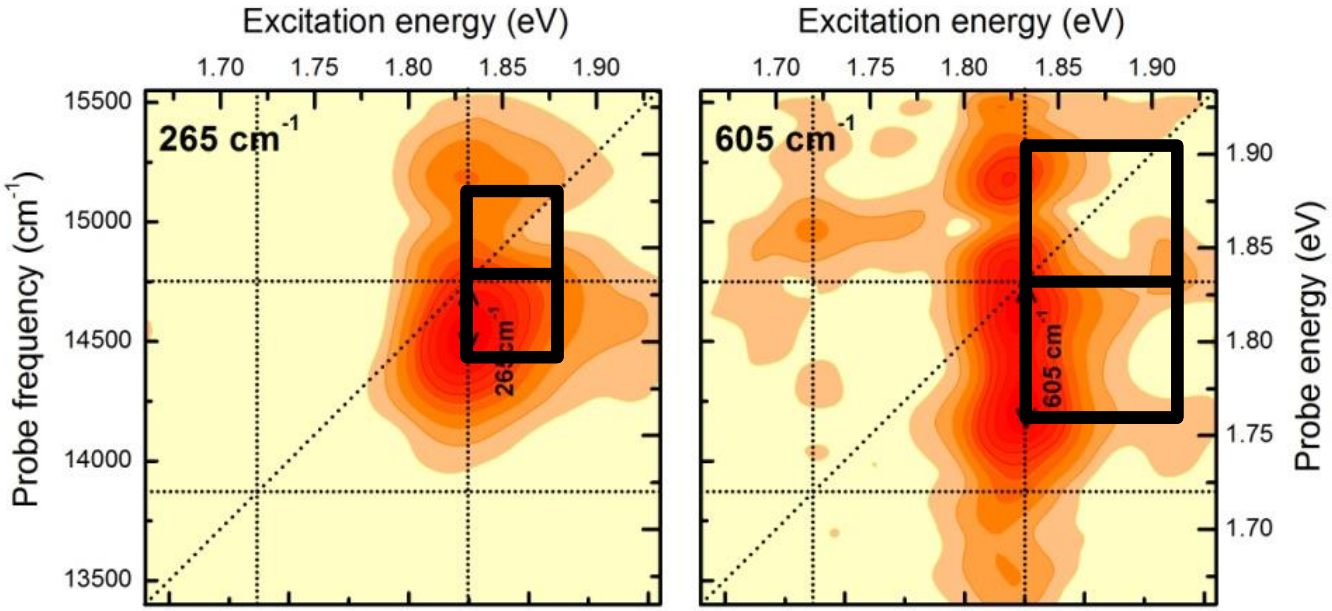


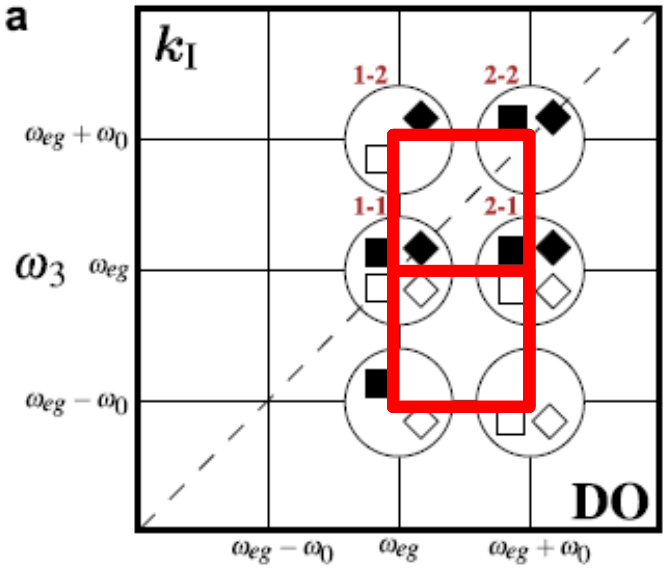


Electronic transitions are 'dressed' with vibrations.

Egorova, *JCP* 2008
Butkus et al, *CPL* 2012

Beating map for low-energy vibrational modes

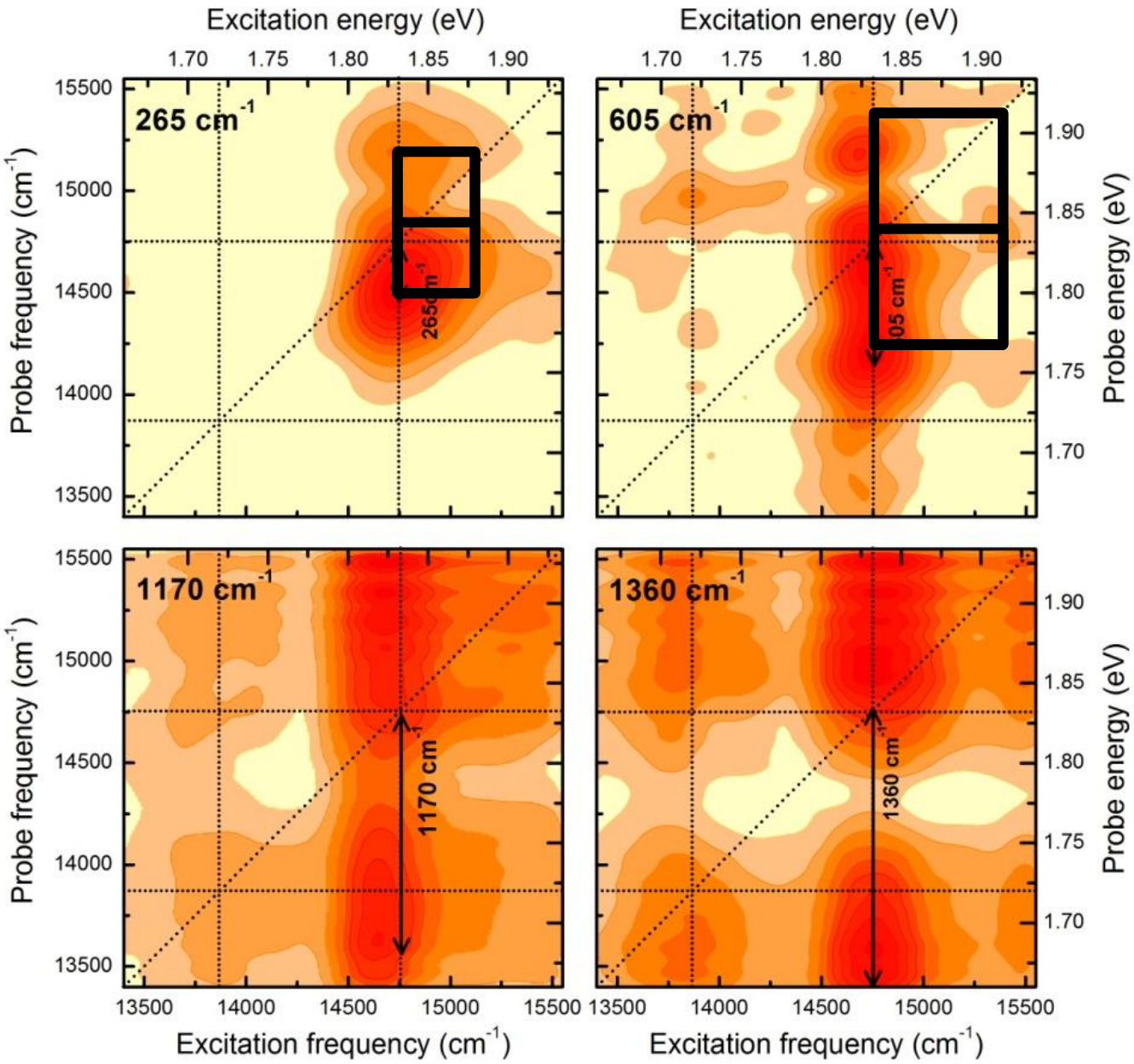




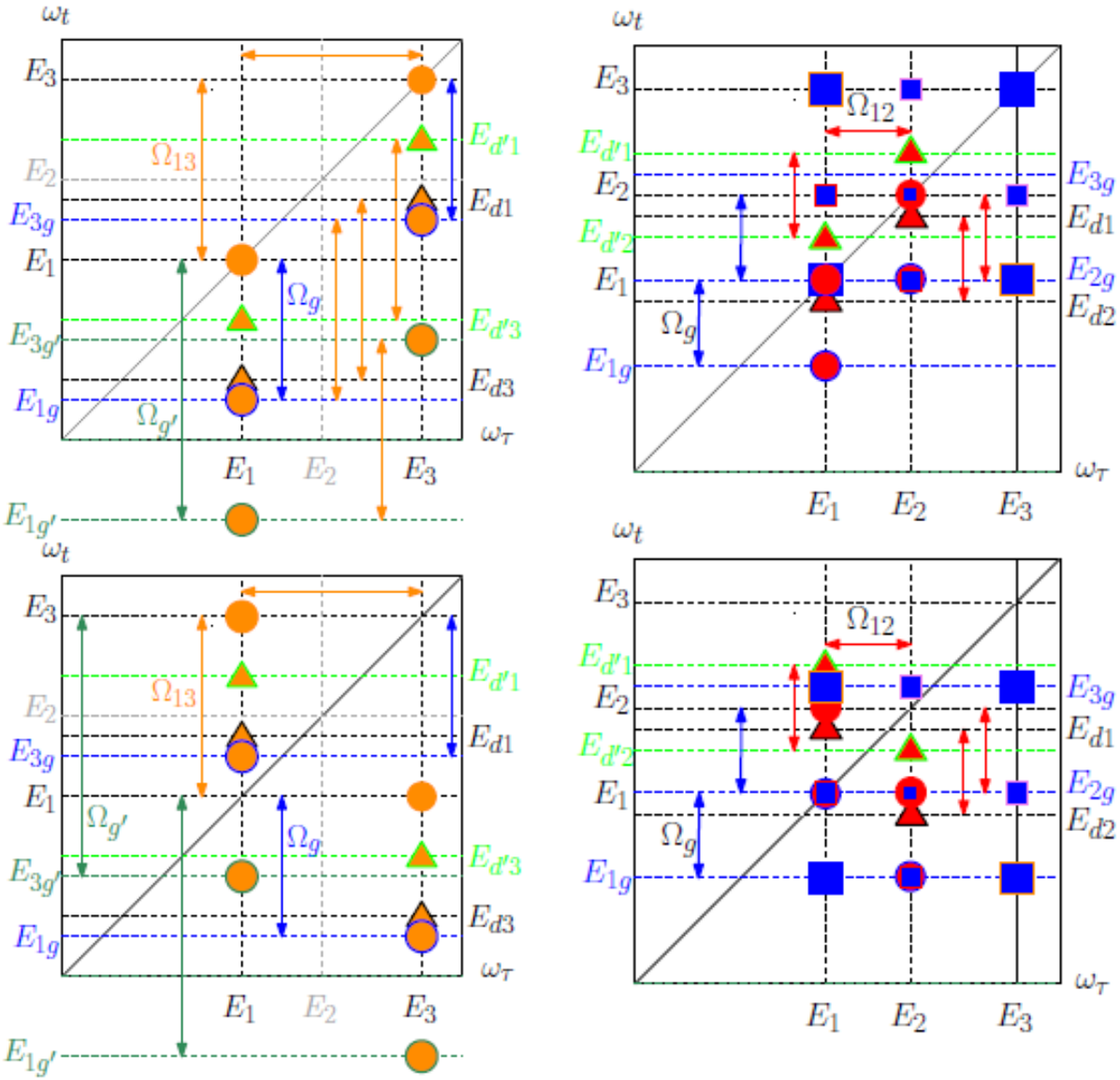
Electronic transitions are 'dressed' with vibrations.

Egorova, *JCP* 2008
Butkus et al, *CPL* 2012

High-frequency modes disaster

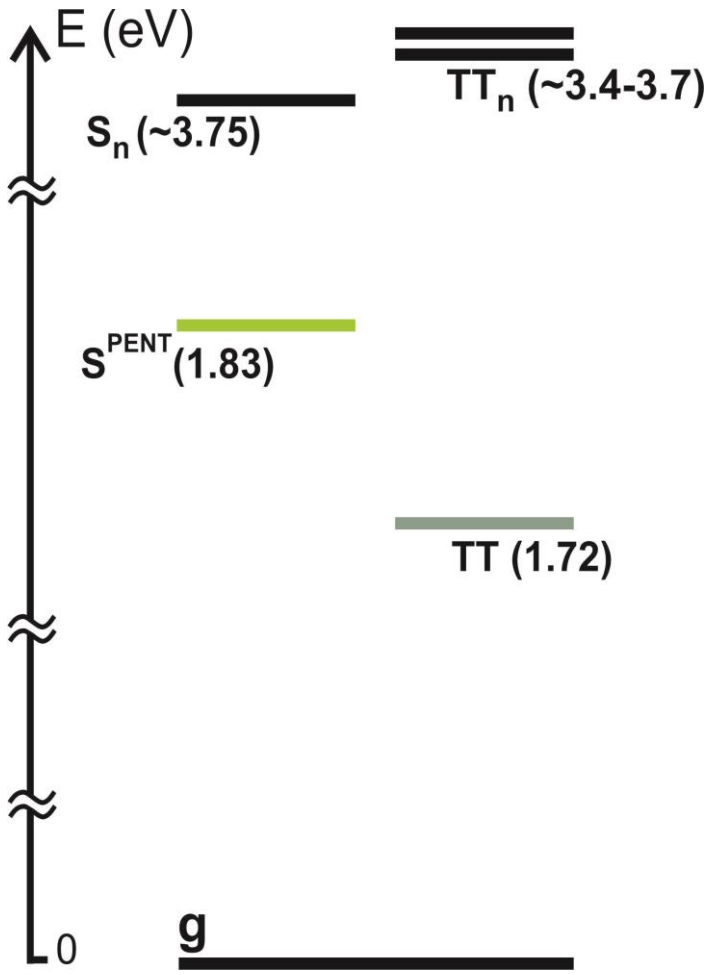


Separating ground and excited state coherences

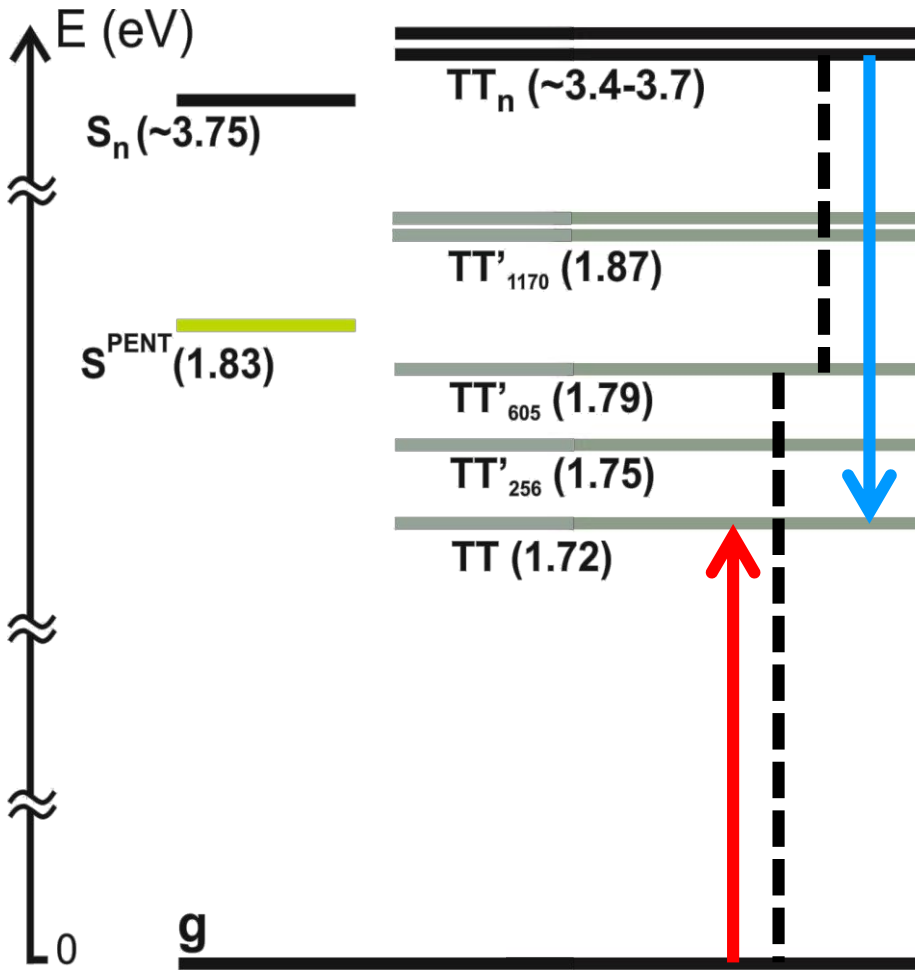


Egorova, *Self-Analysis of Coherent Oscillations in Time-Resolved Optical Signals,* *J Phys Chem A, (2014)*

Vibronic manifold of multiexciton TT state



Vibronic manifold of multiexciton TT state



$|TT><TT|$

$|TT_3><TT|$

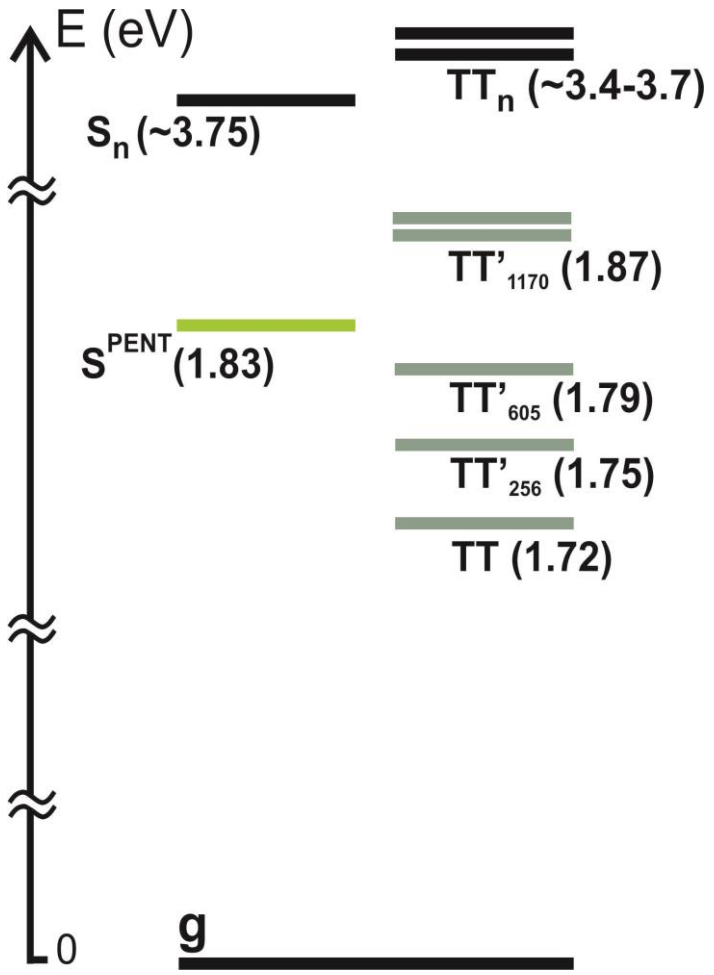
$|TT'><TT|$

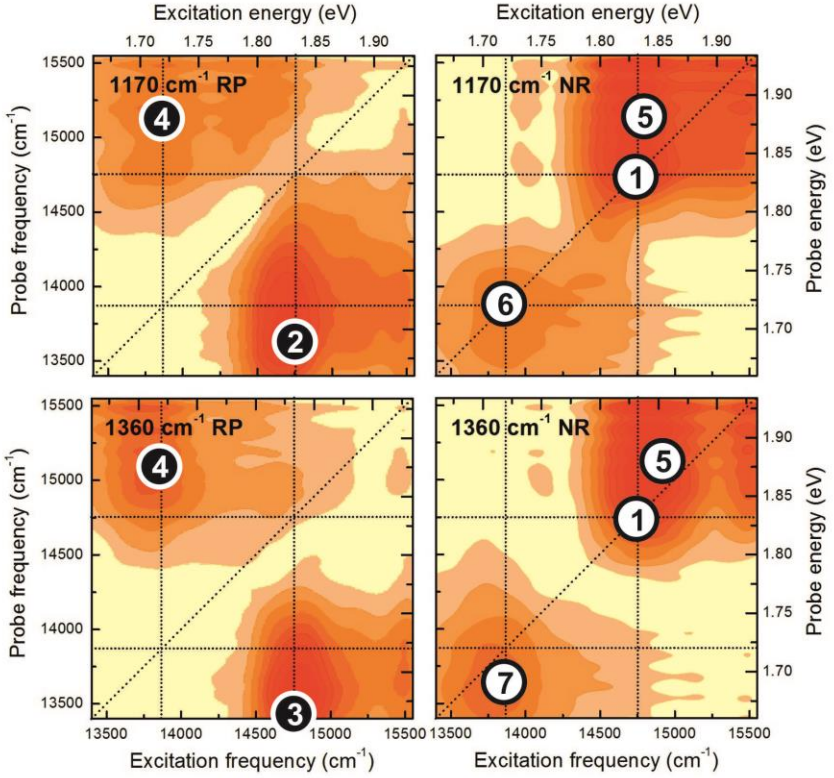
$|g><TT|$

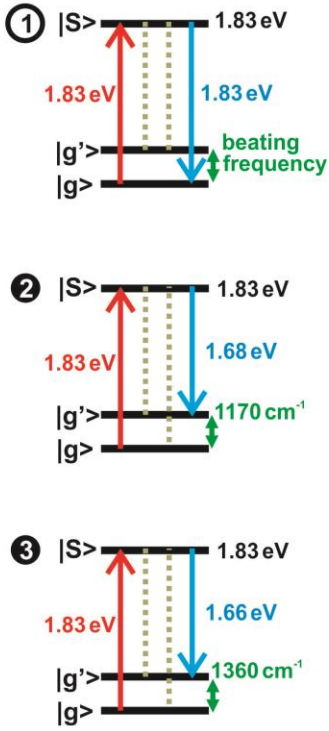
$|g><g|$

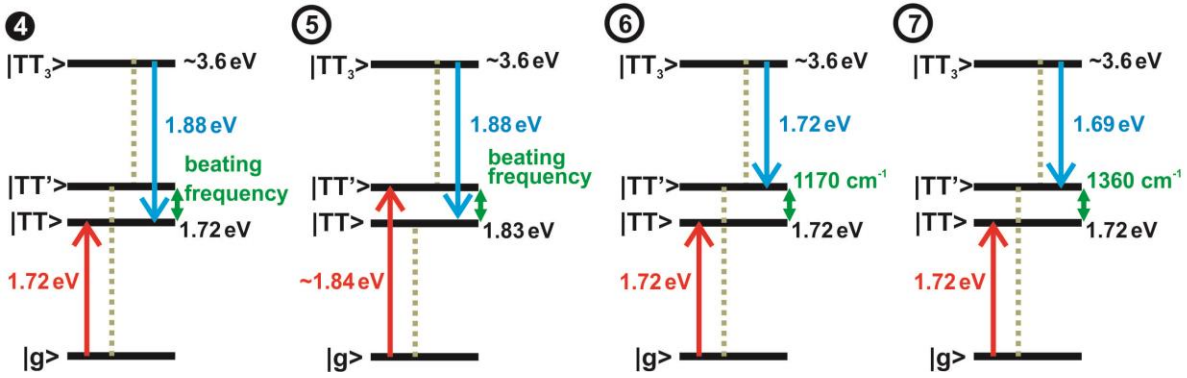
- Bringing vibronic **TT′** states into consideration is essential
- Some **TT′** would mix with **S** and become bright

1. Positions of all peaks can be predicted



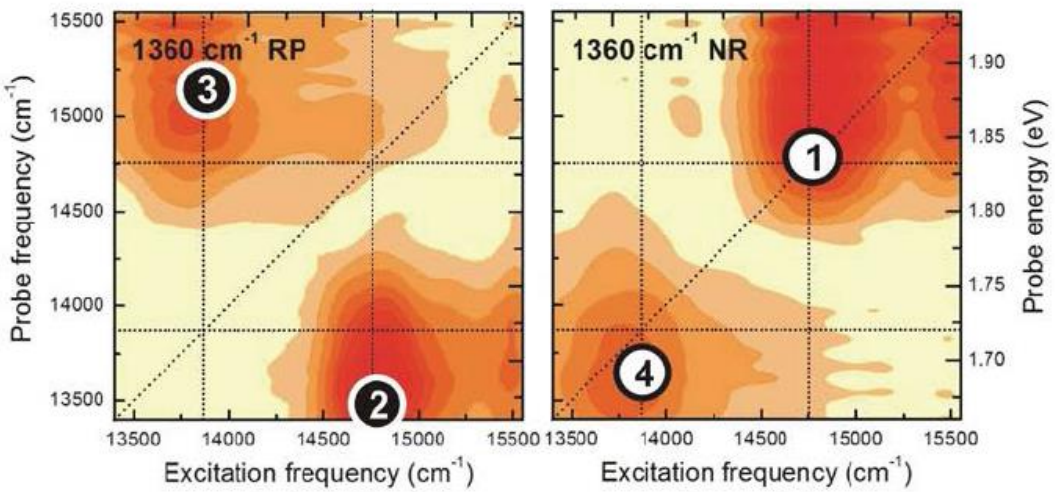


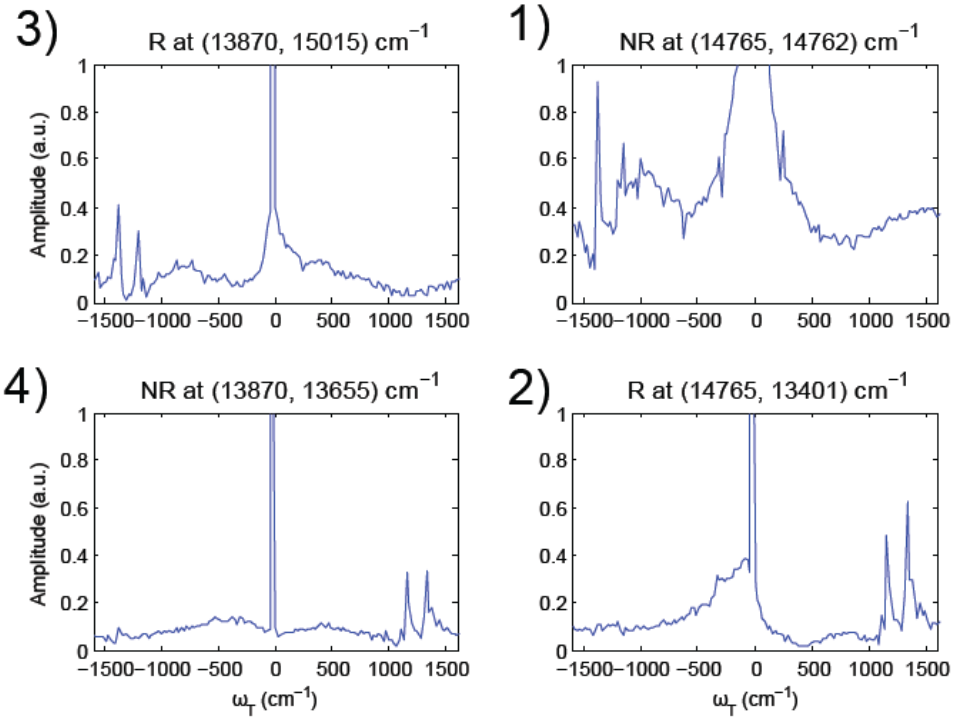




Bright TT' explains all new peaks in the data…

2. Phase analysis





3) ESA (R upper cross-peak)

$|TT><TT|$
$|T_n><TT|$
$|TT'><TT|$ $-\omega_T$
$|g><TT|$
$|g><g|$

1) GSB (NR upper diagonal peak)

$|g><g|$
$|S><g|$
$|g'><g|$ $-\omega_T$
$|S><g|$
$|g><g|$

4) ESA (NR lower diagonal peak)

$|TT'><TT'|$
$|T_n><TT'|$
$|TT><TT'|$ $+\omega_T$
$|TT><g|$
$|g><g|$

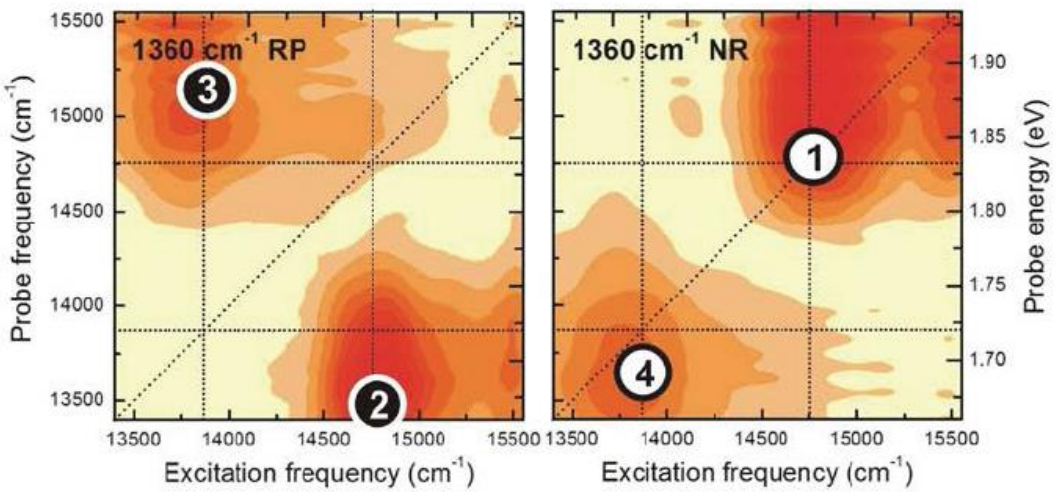
2) GSB (R lower cross-peak)

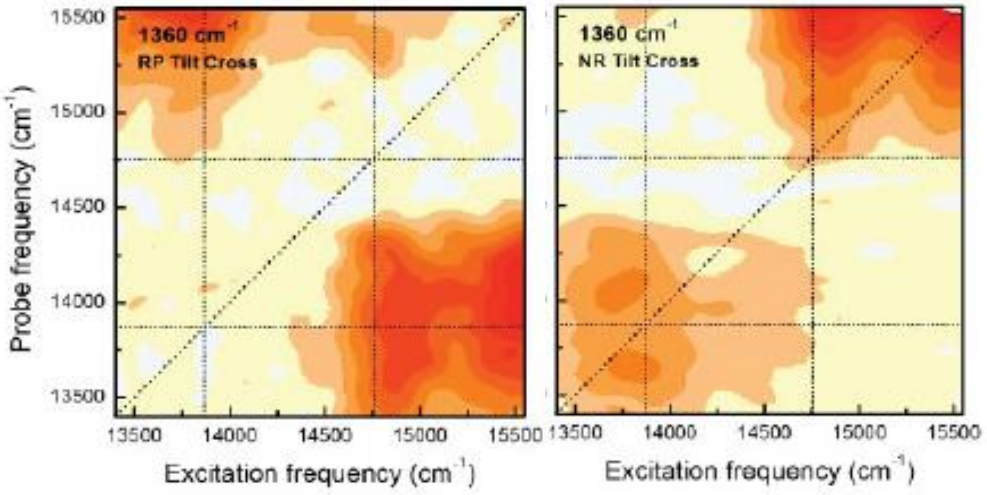
$|g'><g'|$
$|S><g'|$
$|g><g'|$ $+\omega_T$
$|g><S|$
$|g><g|$

Using both Re and Im part of 2D spectra to verify pathways

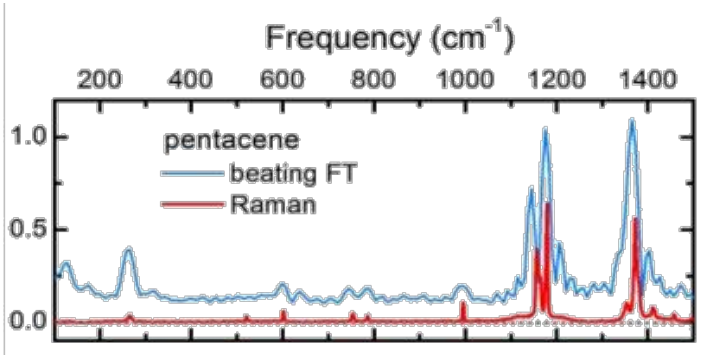
Seibt & Pullerits, JPCC 2013
Li, Cundiff et al, Nat Com 2013
Song, Scholes et al, JCP 2015

3. Polarisation suppression of GS coherences

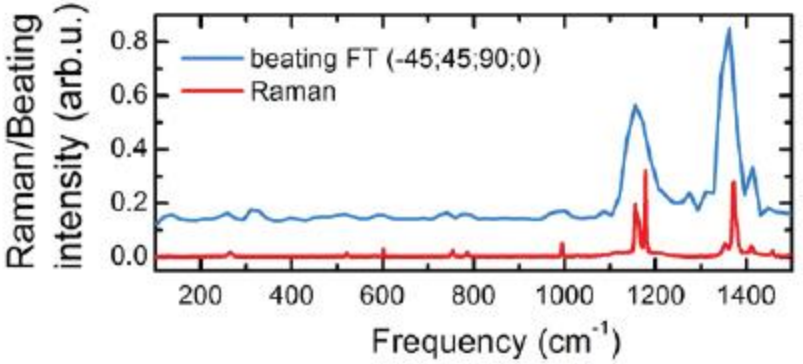




(0,0,0,0)



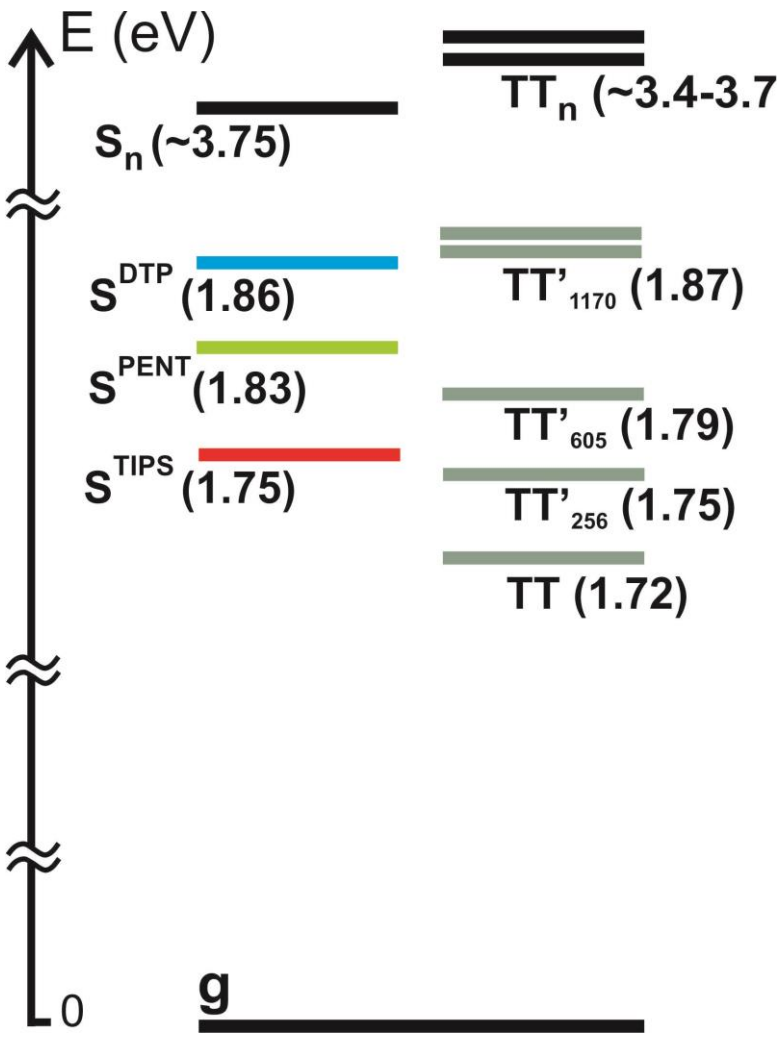
(0,90,45,-45)

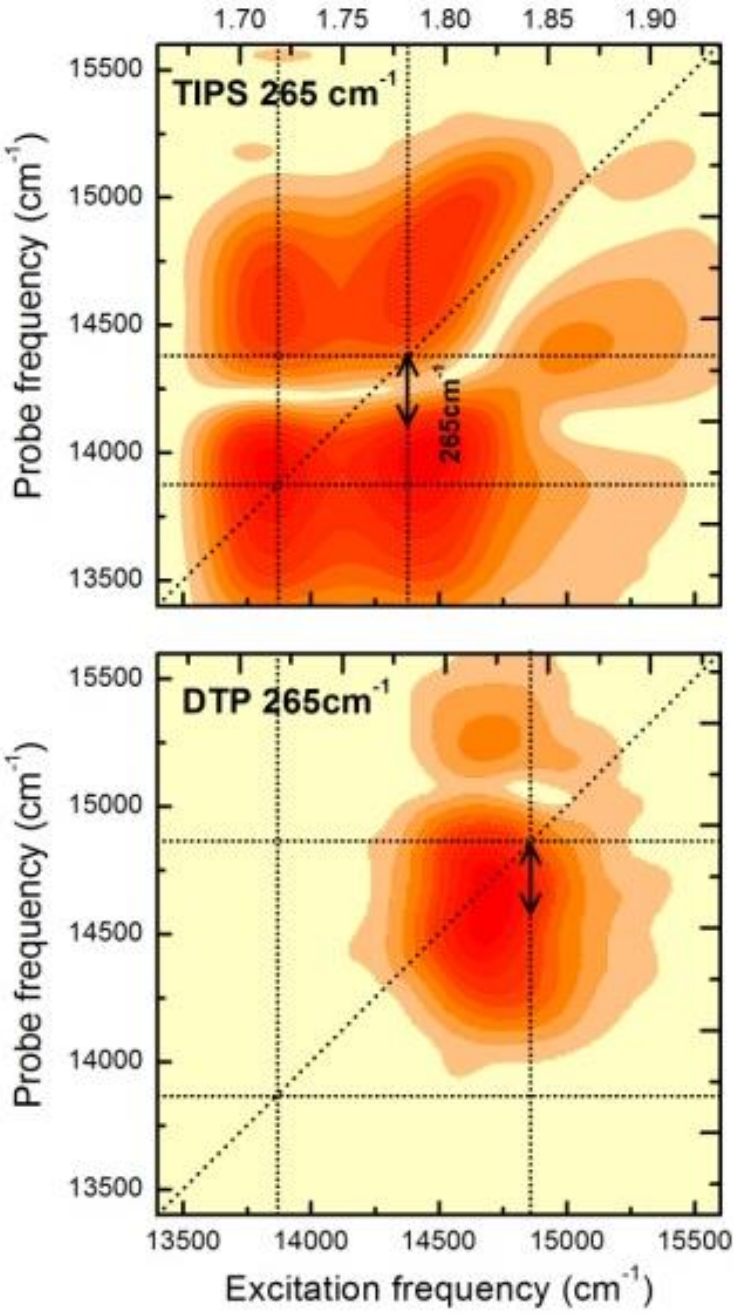


Peaks 2-4 involve additional state apart from Singlet

Zanni et al, PNAS 2001
Schlau-Cohen et al, Nat Chem 2012

4. S – TT mixing in TIPS and DTP pentacene...



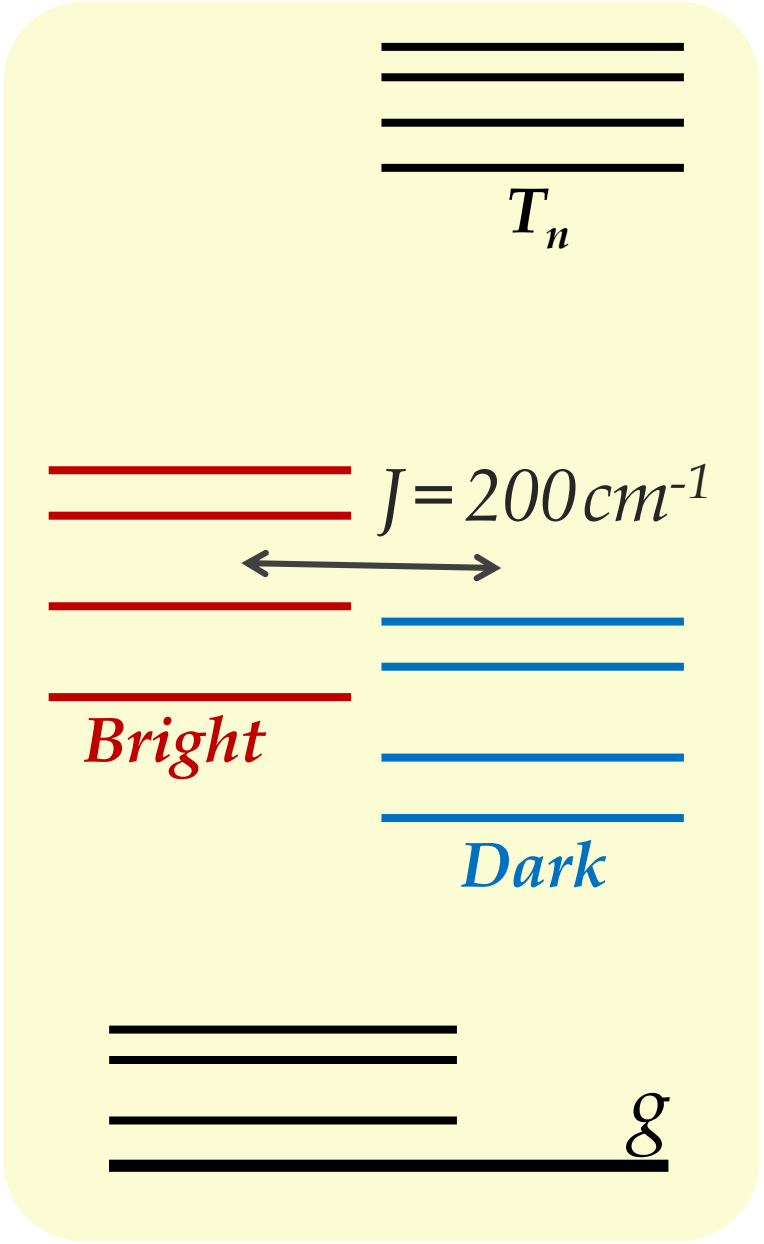


- Even low frequency vibronic modes of TIPS are mixed with singlet state

5.Modelling of SF 2D spectra and dynamics

The model:

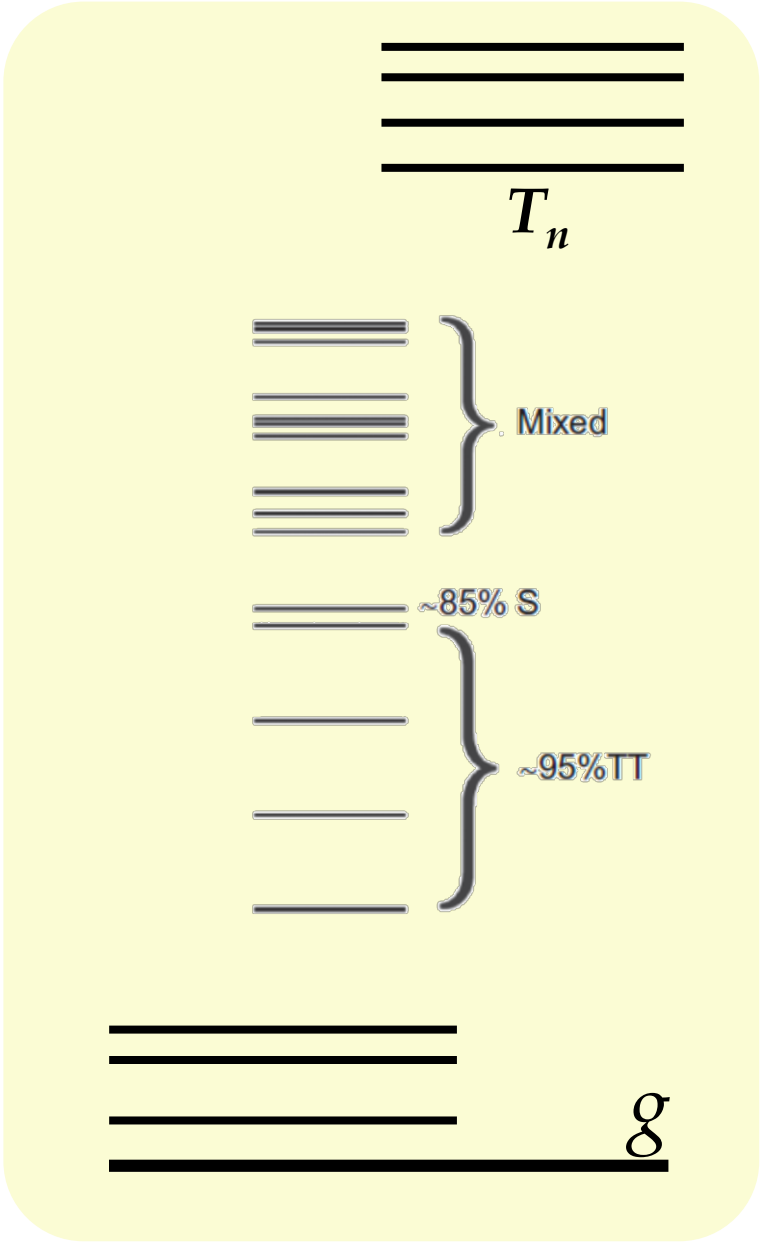
- Four diabatic electronic states
- Vibronic manifolds of 3 modes (265, 1170, 1360 cm^{-1})
- Weak coupling of 200 cm^{-1}
- Weak harmonic bath



Modelling of fission 2D spectra and dynamics

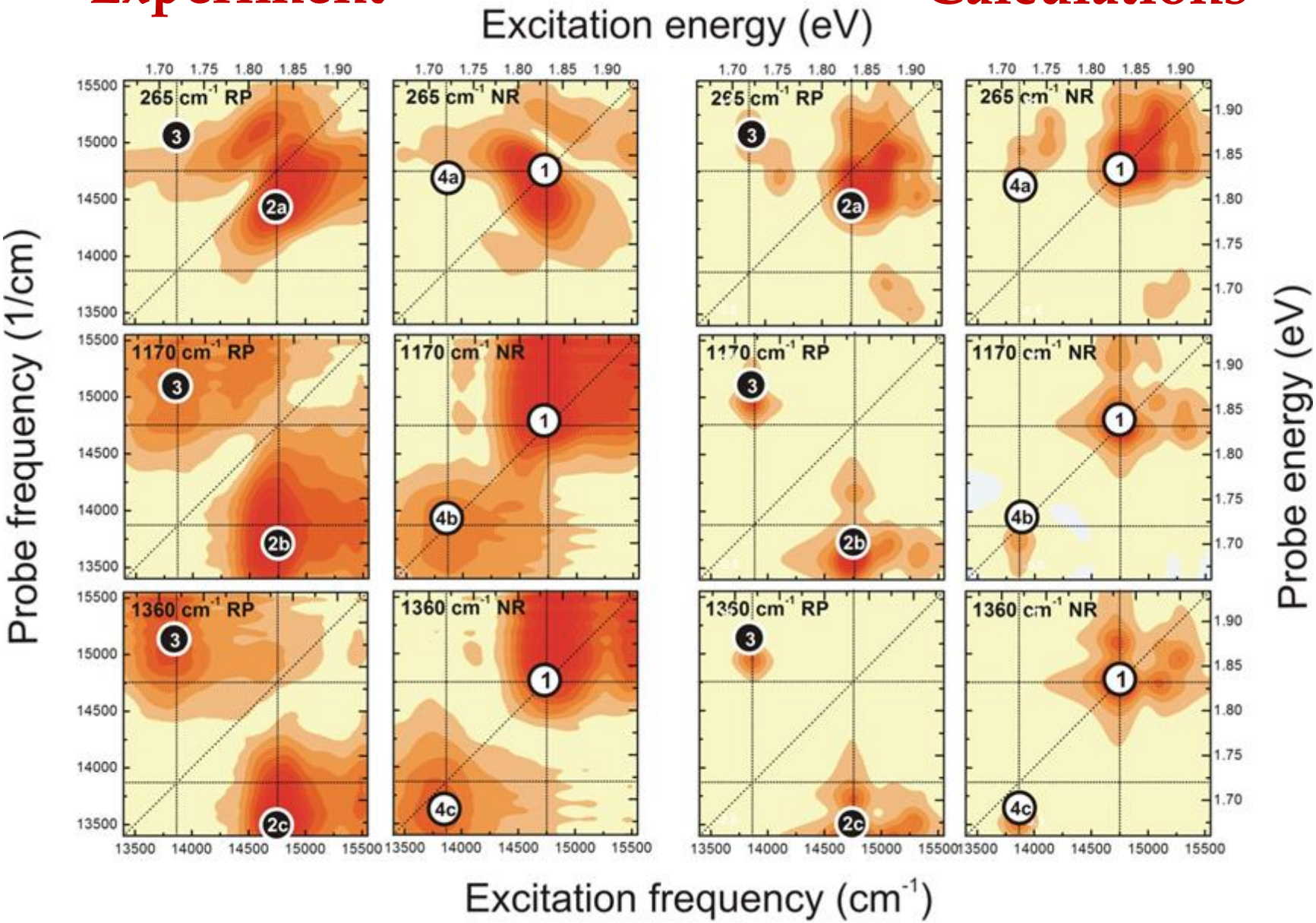
The model:

- Four diabatic electronic states
- Vibronic manifolds of 3 modes (265, 1170, 1360 cm^{-1})
- Weak coupling of 200 cm^{-1}
- Weak harmonic bath

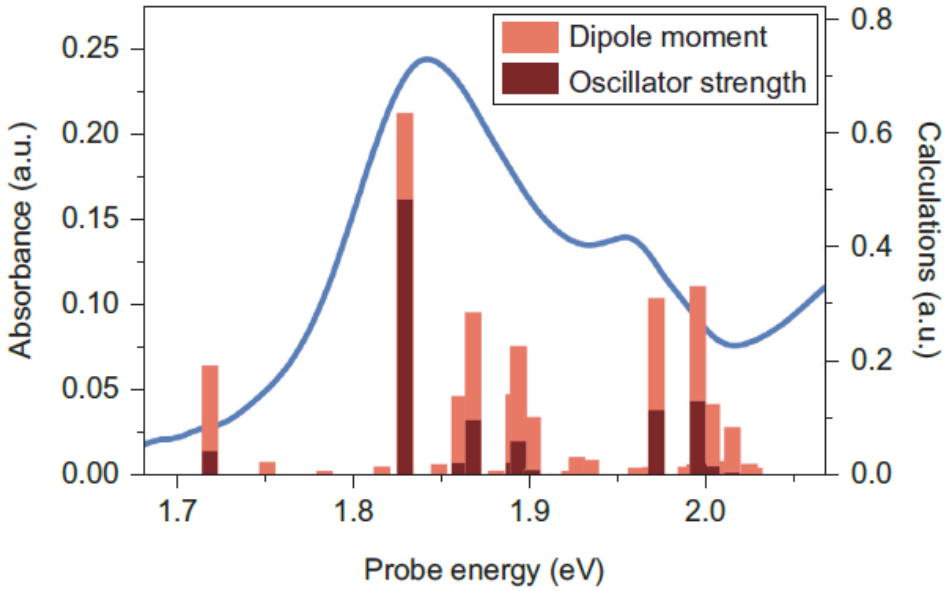


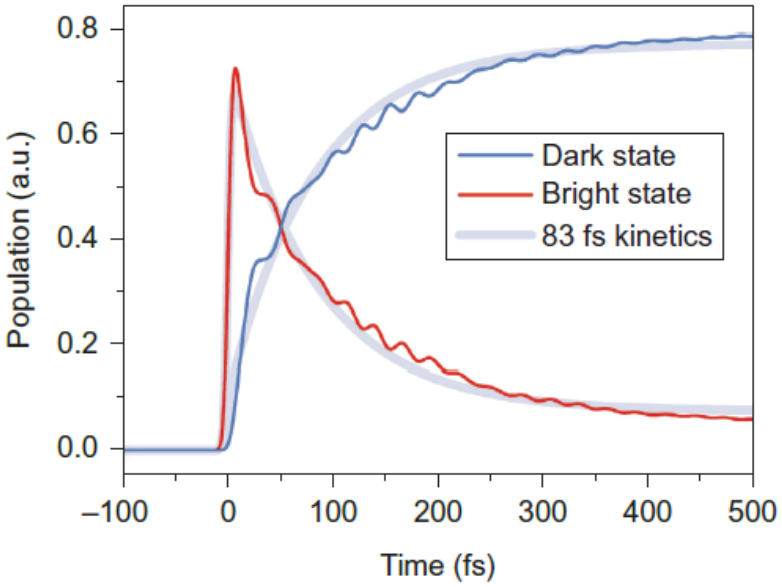
Modelling of 2D spectra

Experiment **Calculations**



Modelling of absorption & fission dynamics

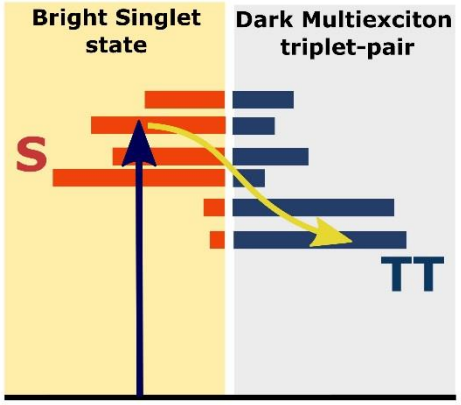




Conclusions for pentacene-based crystals:

- Mixing between vibronic manifolds of S and TT promotes fast Singlet Fission

- Vibrations add to the Density of States and accelerate charge/energy transfer in organic materials



Optical control of electronic devices

David Cahen

FOM Institute AMOLF

Yves Rezus

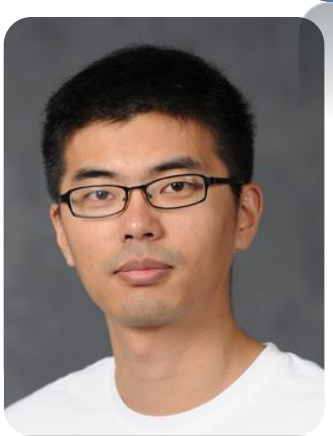
Jean-Luc Bredas

Weizmann Institute of Science

Robert Lovrincic

Slava Coropceanu

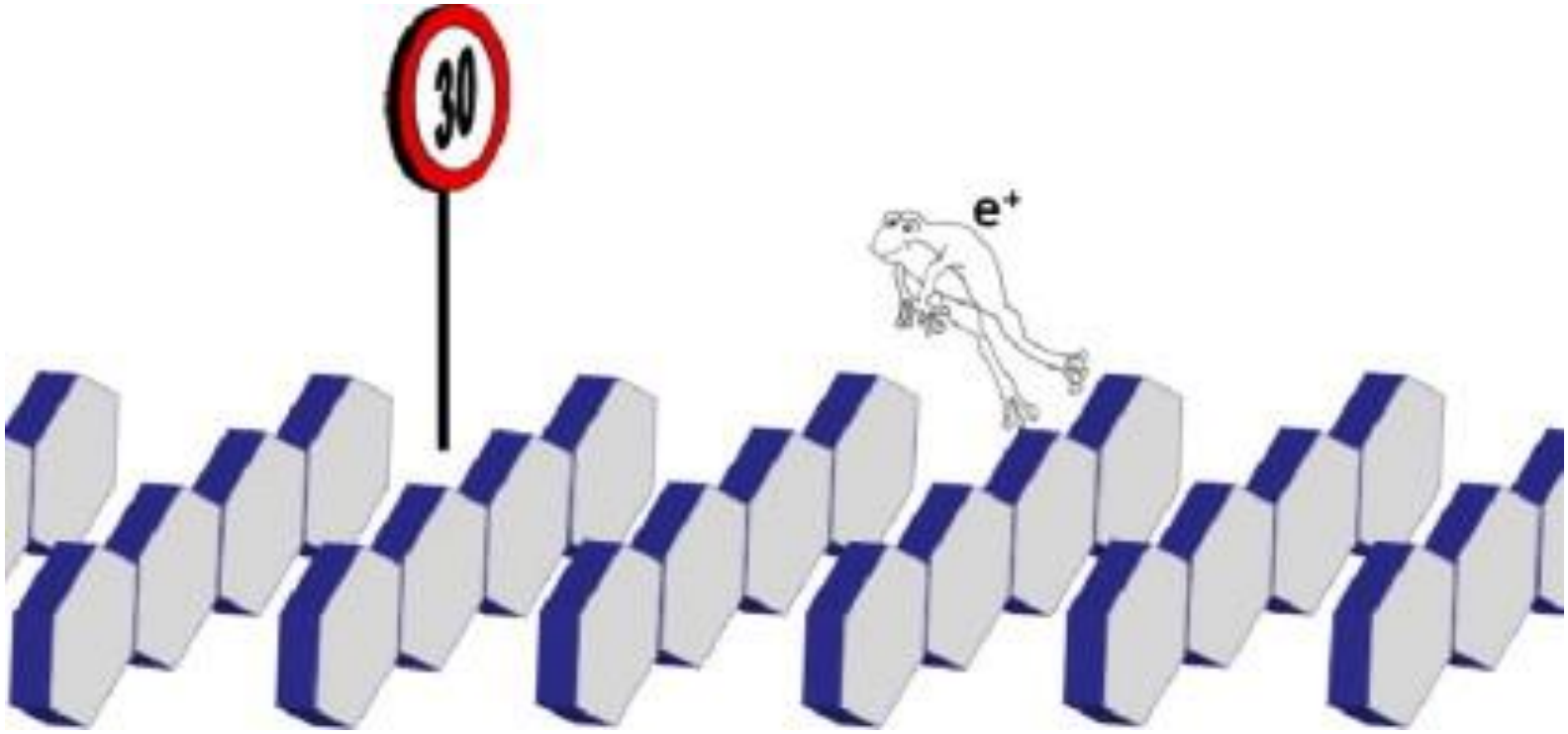
Oleg Selig



Yu Xi

Sasha Fonari

Charge transport in organic materials



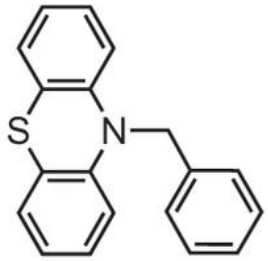
Troisi, *Organic Electronics* (2011)

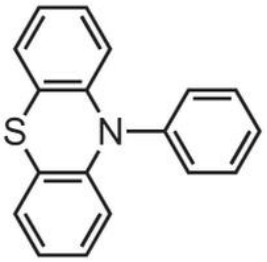
- 'Soft' material with rich structural dynamics
- Weak electronic couplings
- Charges are localised
- Plenty of local (high-frequency) vibrations

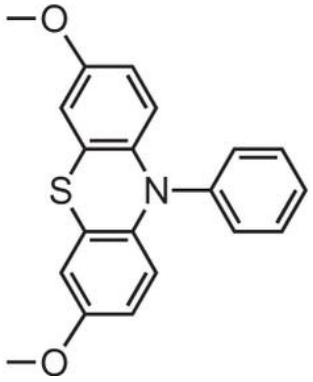
Coupling between the vibrations and transport properties on macroscale

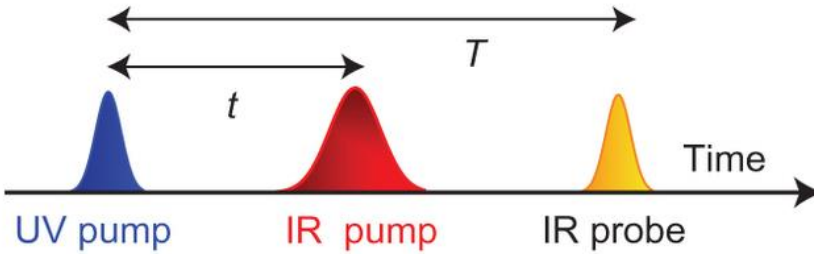
Coupling between vibrations and charge transfer

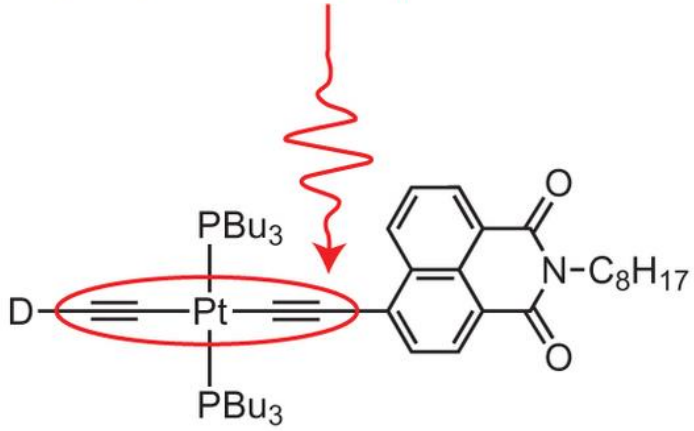
Donor (D) =

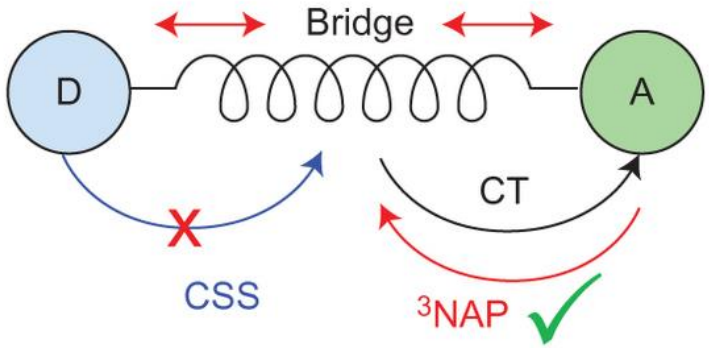






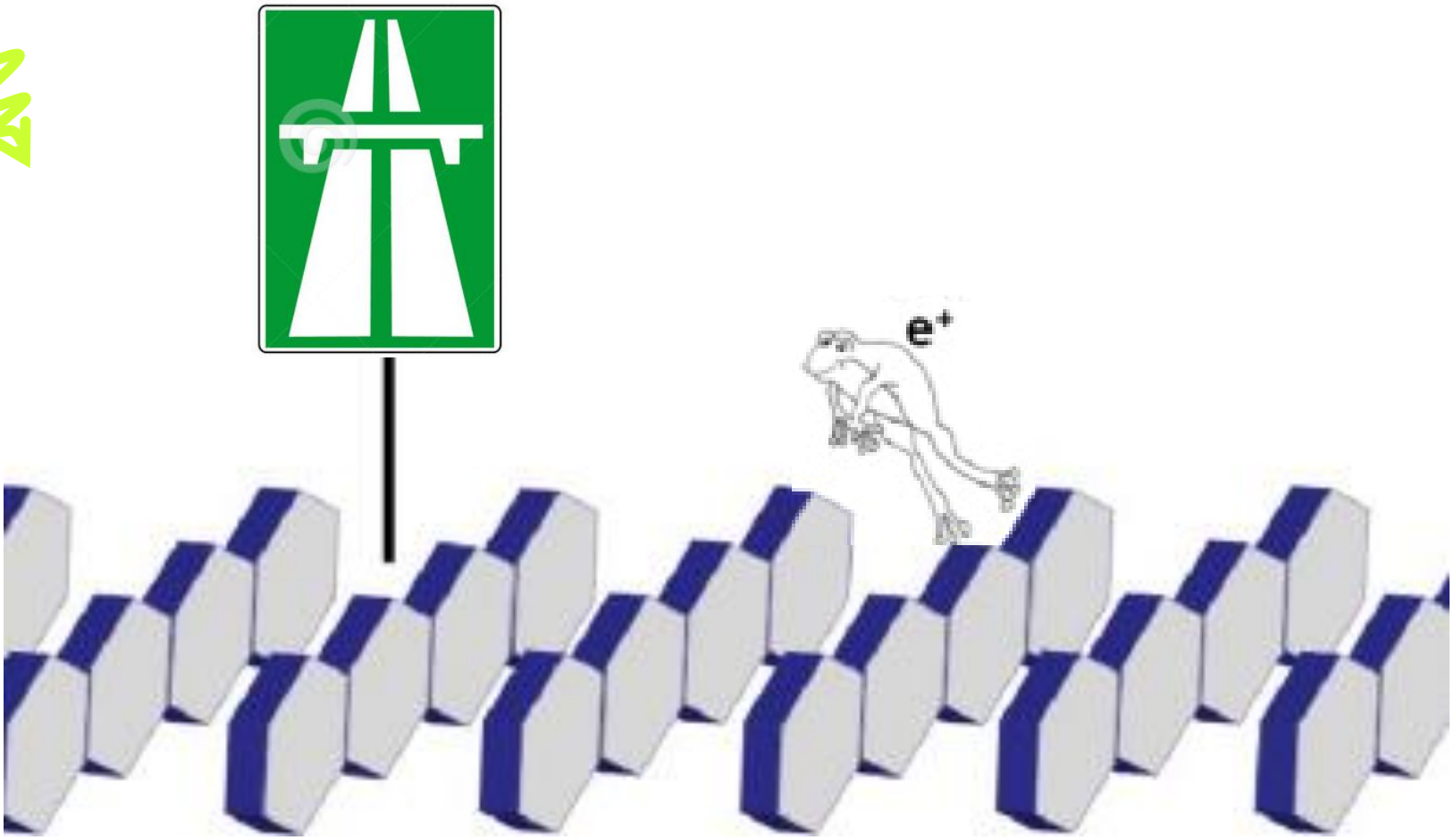






Delor et al, *Science* (2014)
Delor et al, *Nature Chem* (2015)

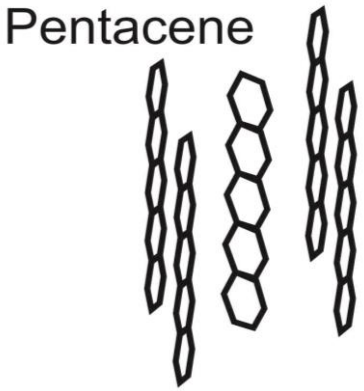
Our goal: to help the frog!



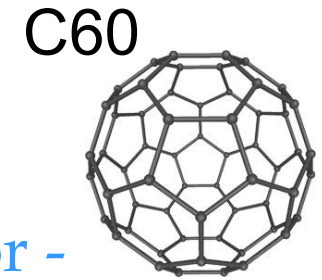
Troisi, *Organic Electronics* (2011)

- As charge transport is sensitive to vibrations – can we use them to control the carriers?
  - Control over device performance…

Model material system – pentacene/C60 bilayer

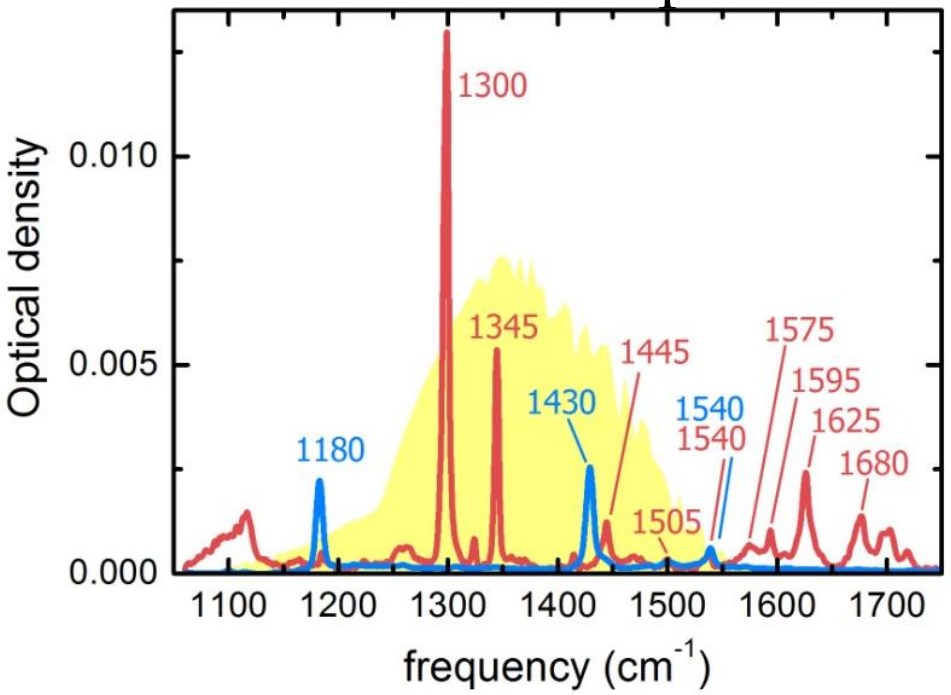


- p-type organic semiconductor
- polycrystaline film

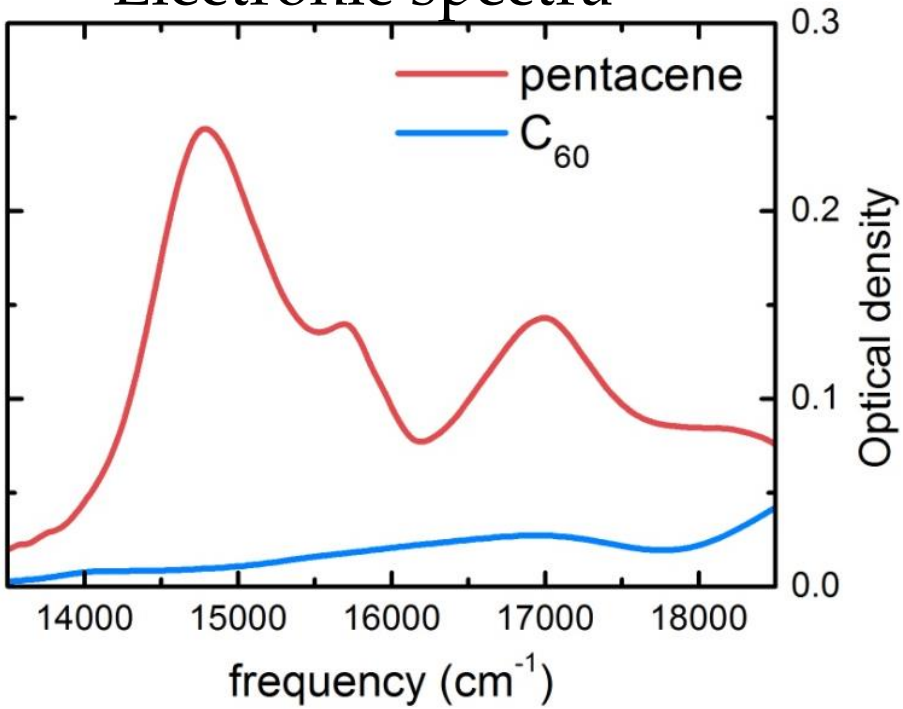


n-type organic semiconductor -
amorphous/polycrystaline film -

Vibrational spectra

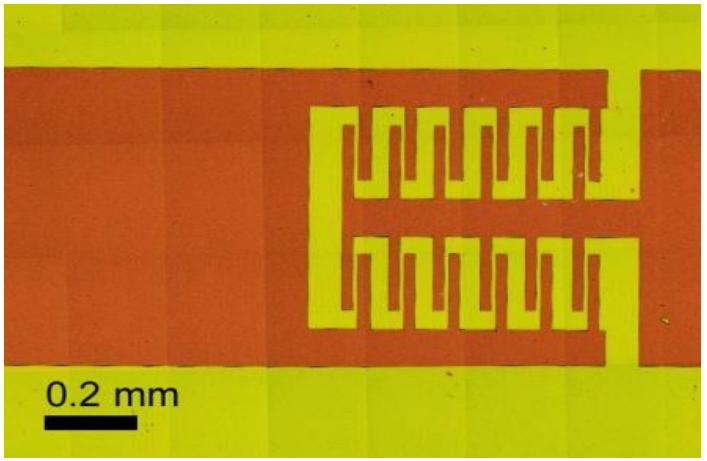


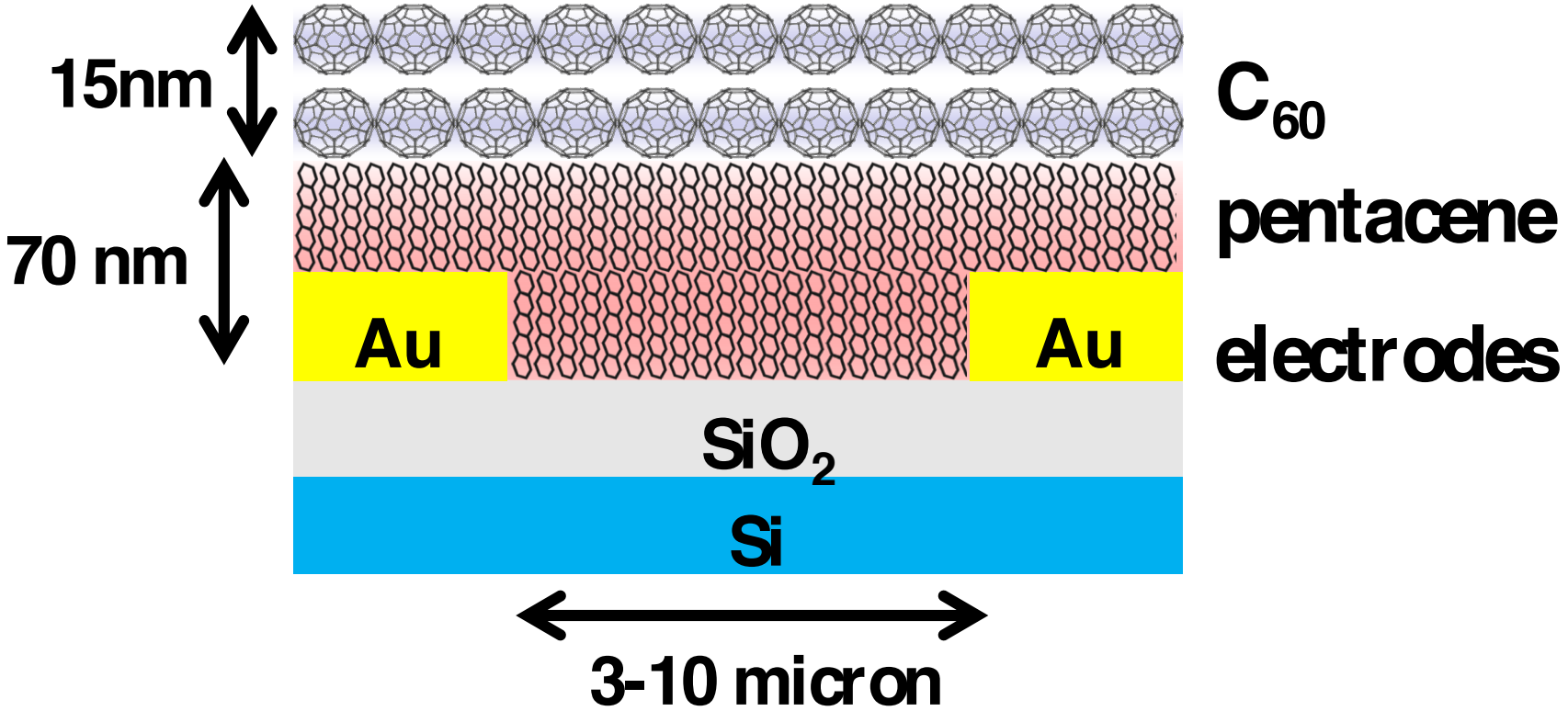
Electronic spectra



Devices

Pentacene/C_{60} photoresistor:

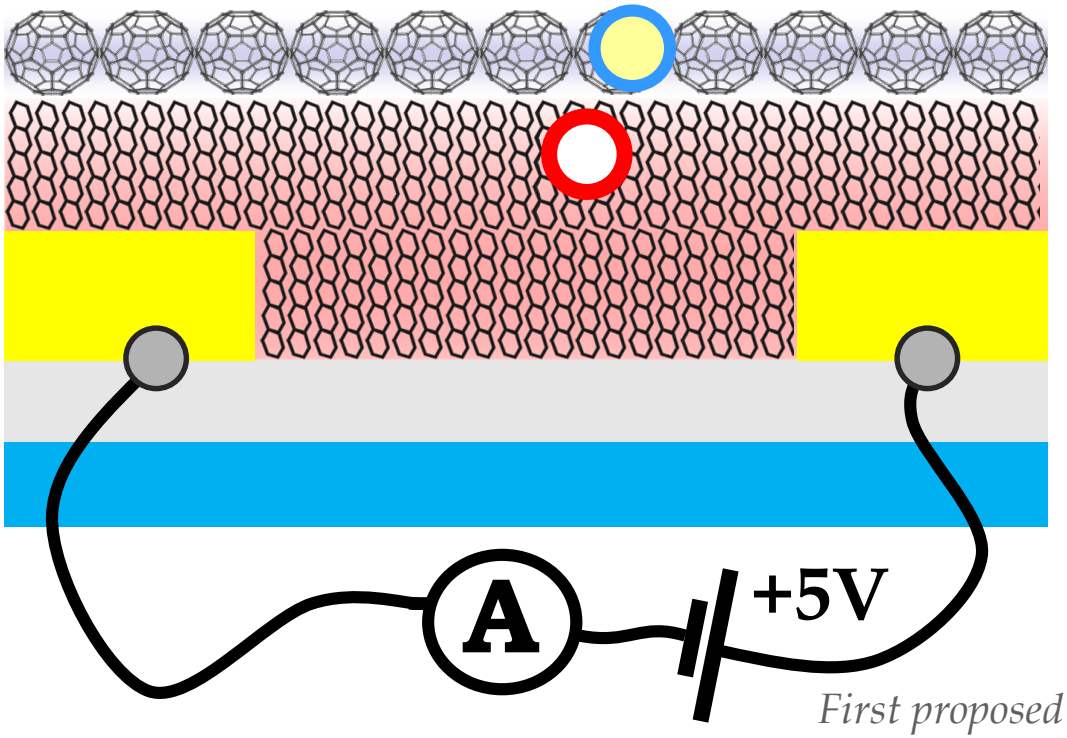




Pump-push photocurrent spectroscopy

1. Create charges
(vis pump pulse)

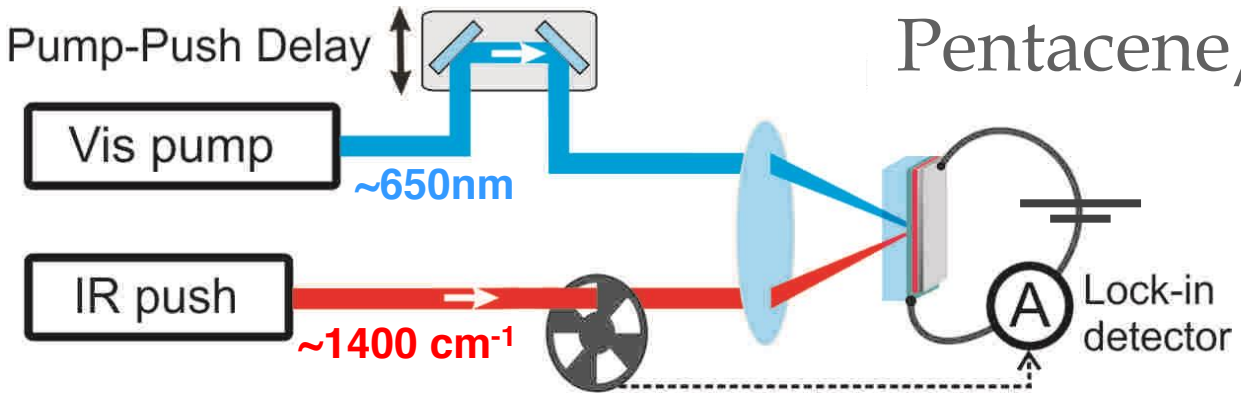
2. Excite vibrations/polarons
(push pulse)



3. Detect the effect
(photocurrent change)

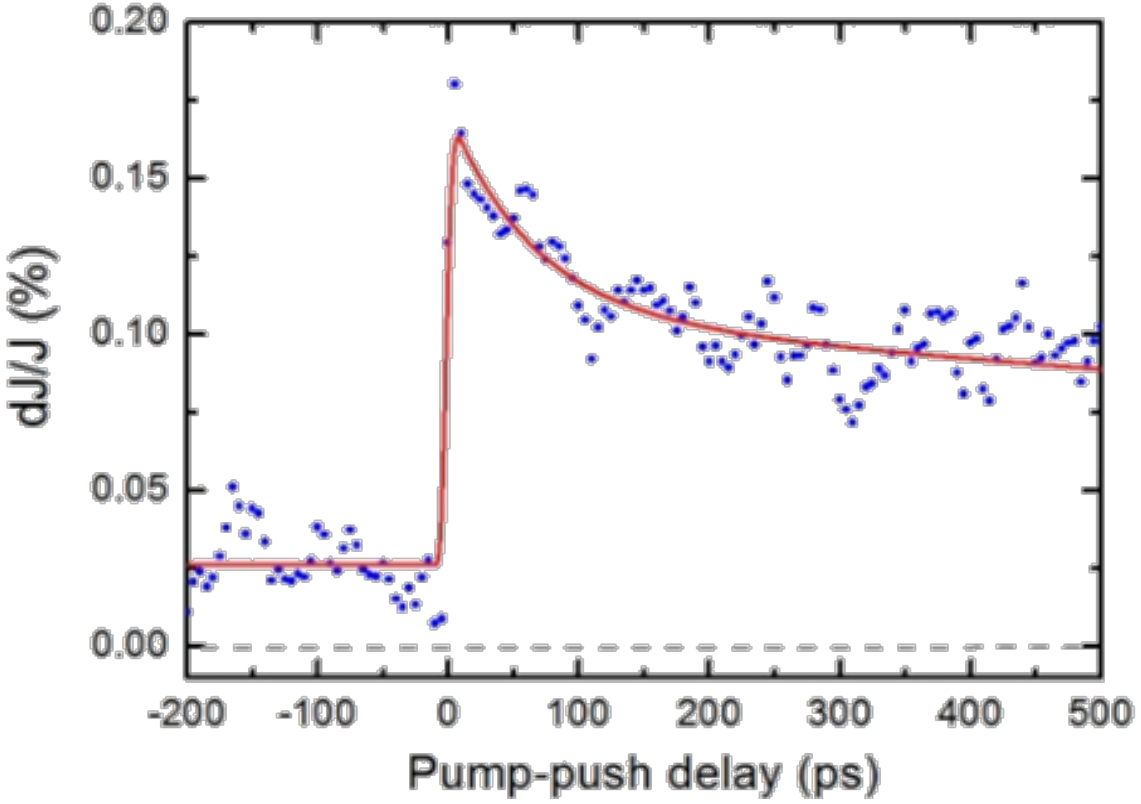
Bakulin et al, Science (2012)
First proposed as a cw experiment: Lukin et al, CPL (1981)
Reintroduced in a time-resolved form with visible push : Frankevich et al, PRB (1999)

Time-resolved spectrally-integrated data

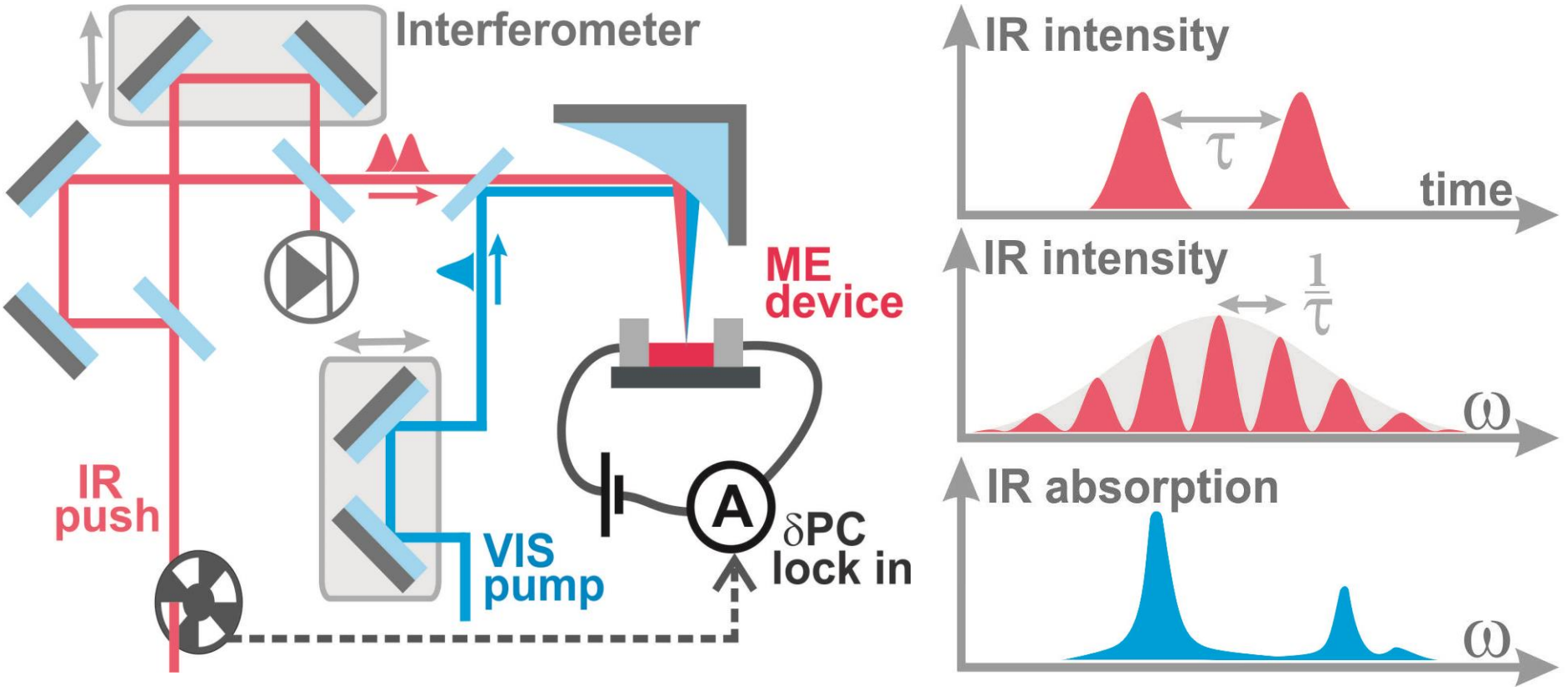


Pentacene/C60 device

- Current increases due to IR excitation
- Substantial response at negative times



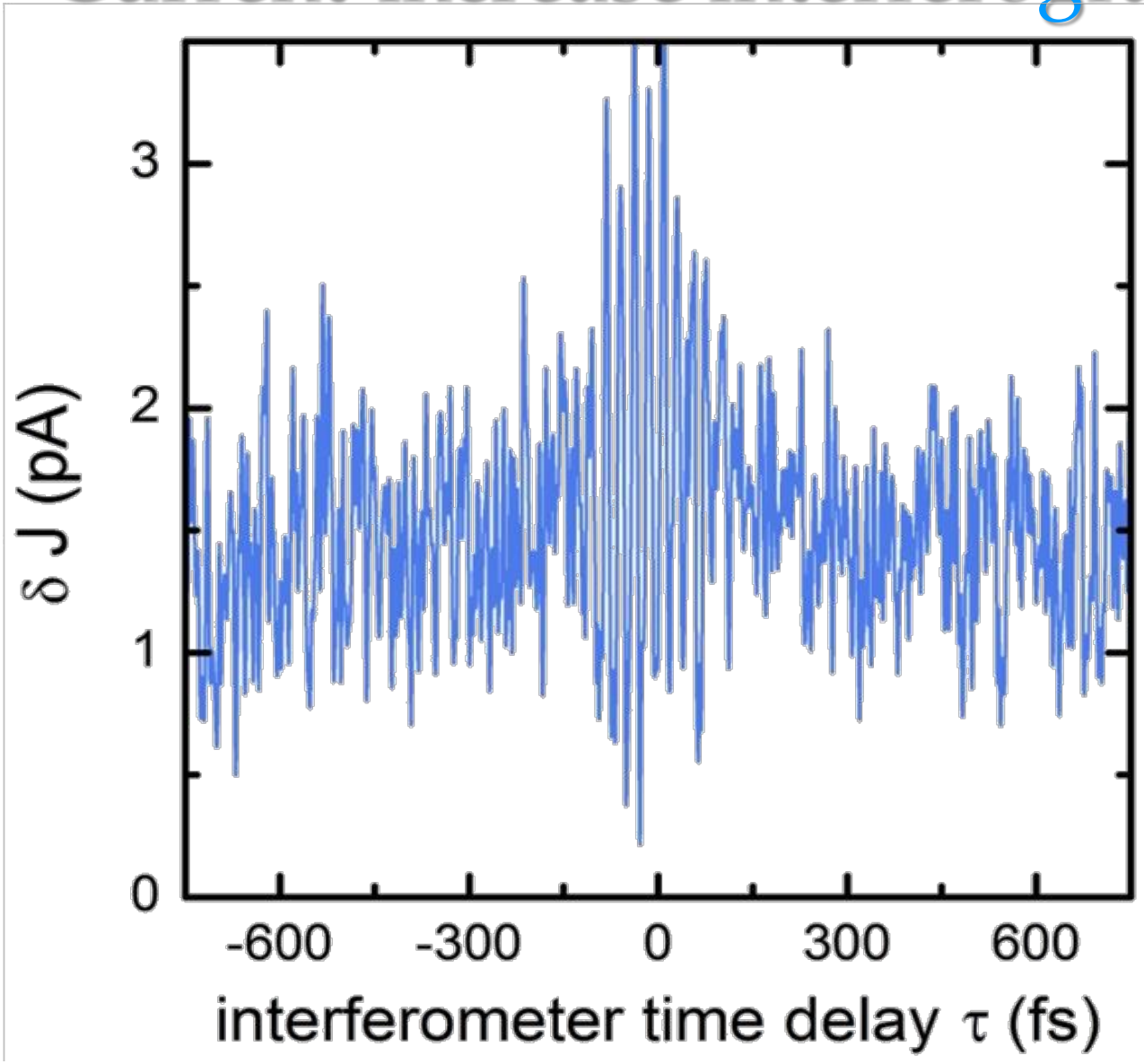
Setup for frequency-resolved measurements



- Interferometer is added to the push-beam path
- This allows for frequency shaping of IR-push beam

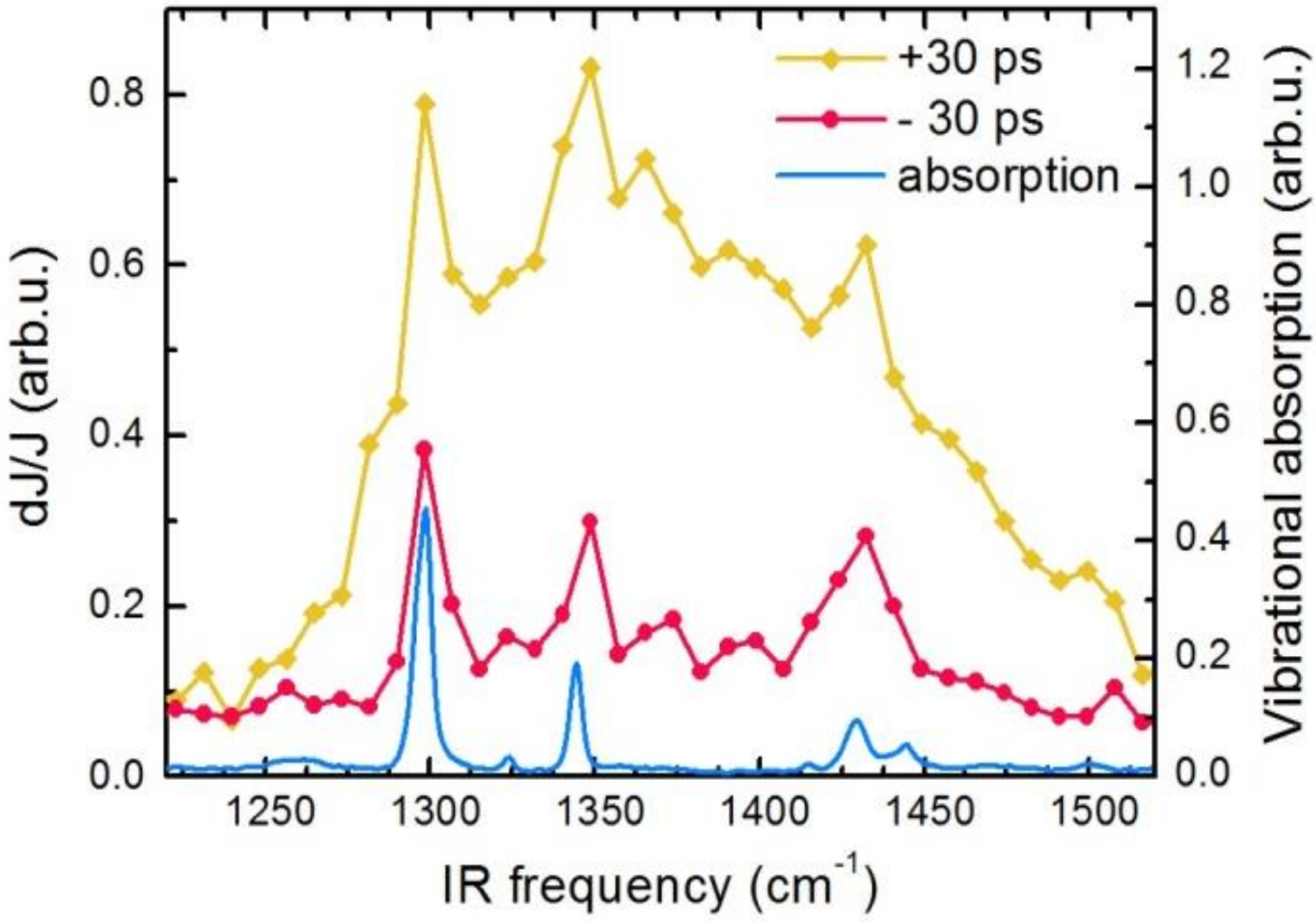
Fast collinear interferometry by Zanni, Tokmakoff & Hamm

Current-increase interferogram



- Measured for differentt pump-push delay times

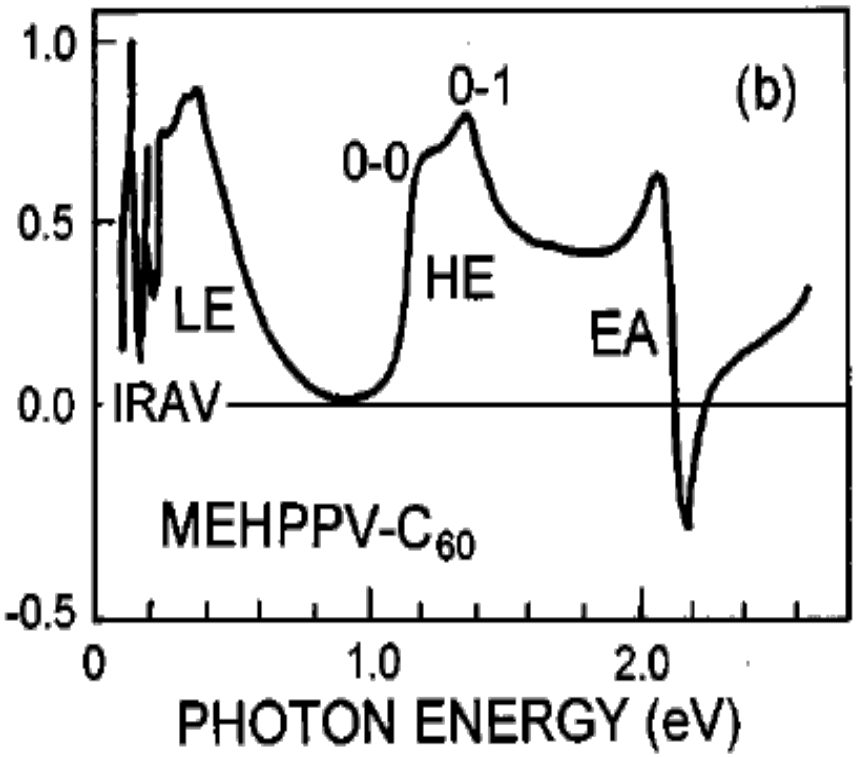
Frequency-resolved data



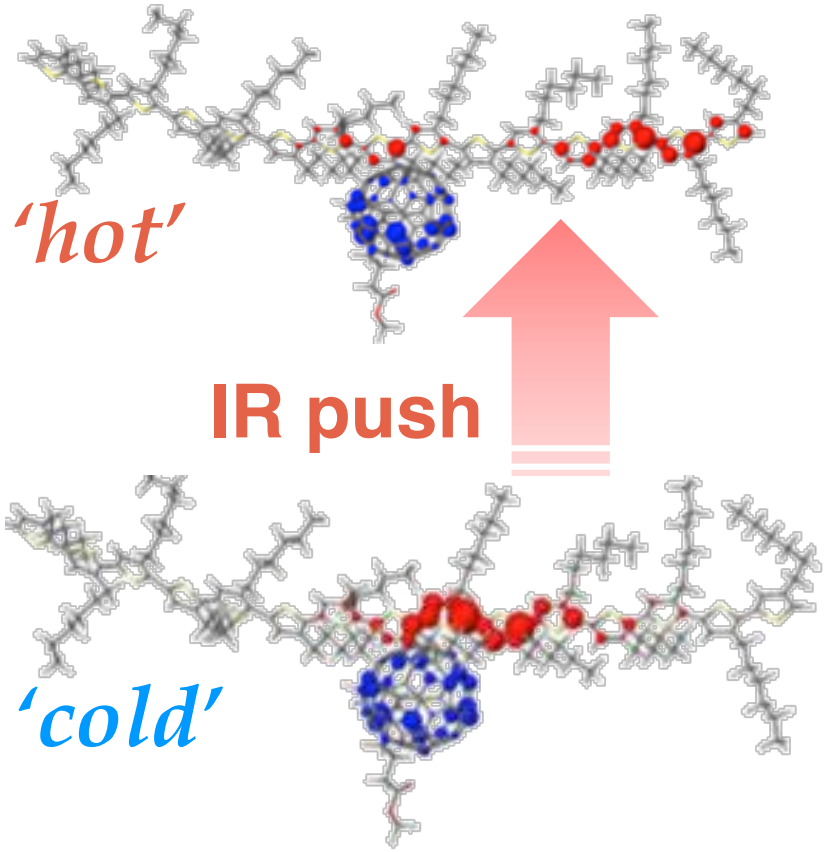
- Broad response – electronic excitation
- Narrow lines – vibrational exicatation

Electronic IR excitation & charge delocalisation

Wei et al, PRB (1996)

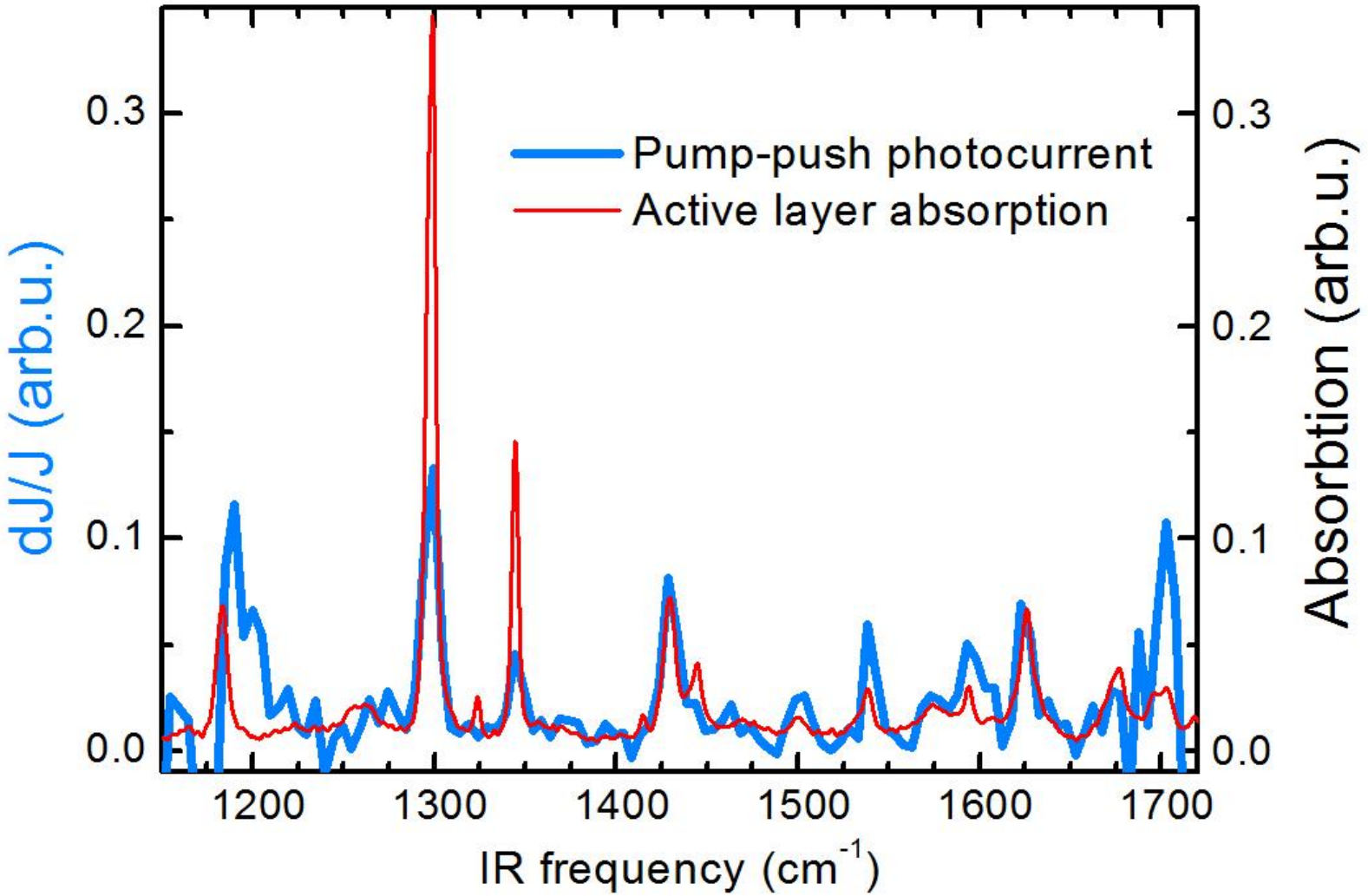


Effect on bound charge pair



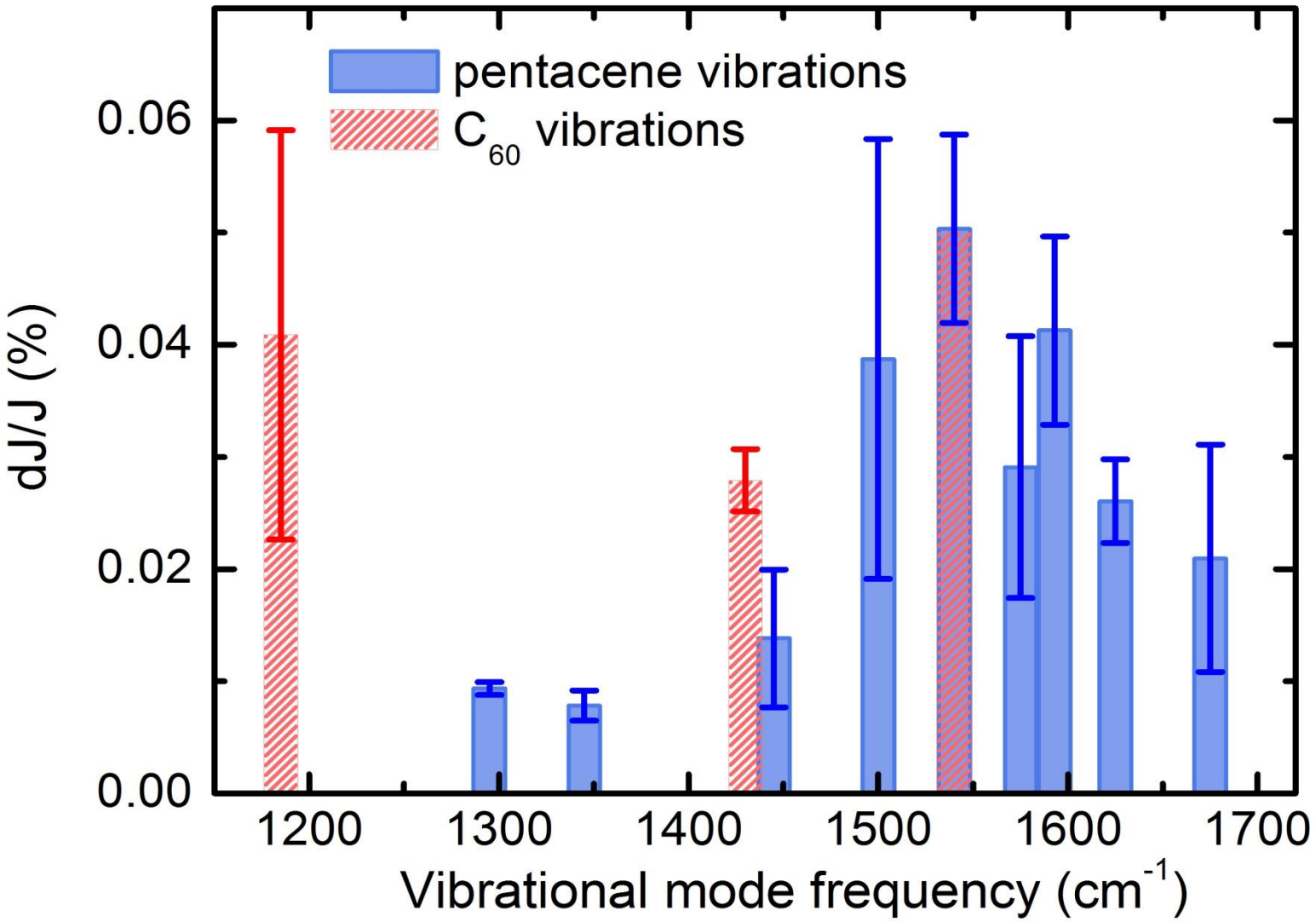
Bakulin et. al, Science (2012)
Dimitrov et. al, JACS (2012)
Bakulin et. al, JPC.Lett. (2013)
Savoie et al.. JACS (2014)

(Time-domain filtered) Vibrational response



- Good correspondence for >10 modes
- Response does not scale with absorbed IR photons

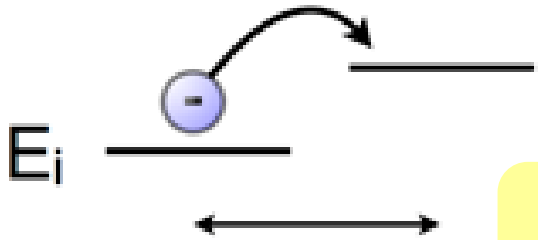
Effect of vibrations on conductivity



- Different ‘coupling’ amplitudes

Why the effect of different modes is different?

MA model



hopping rate

$k \sim v^2 n_D$

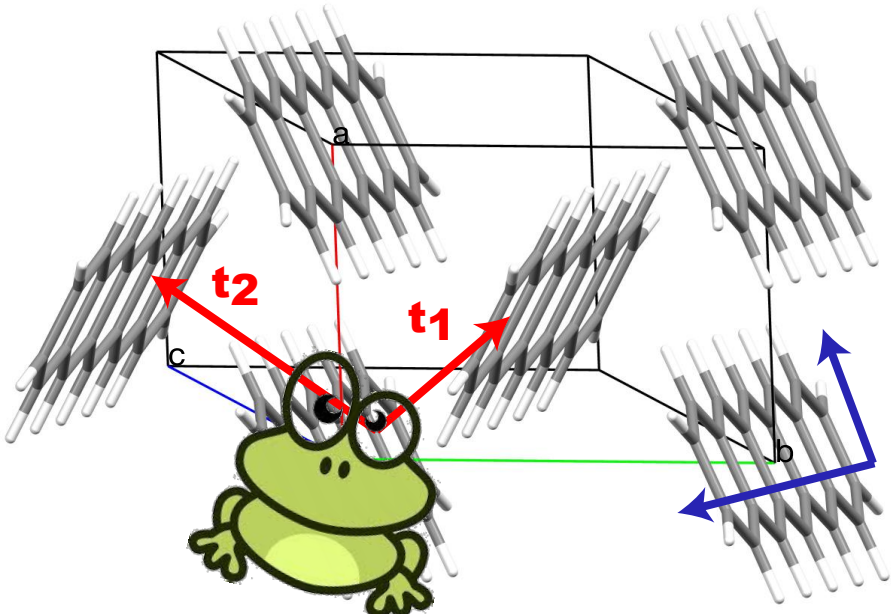
electron-vibrational coupling

occupation number

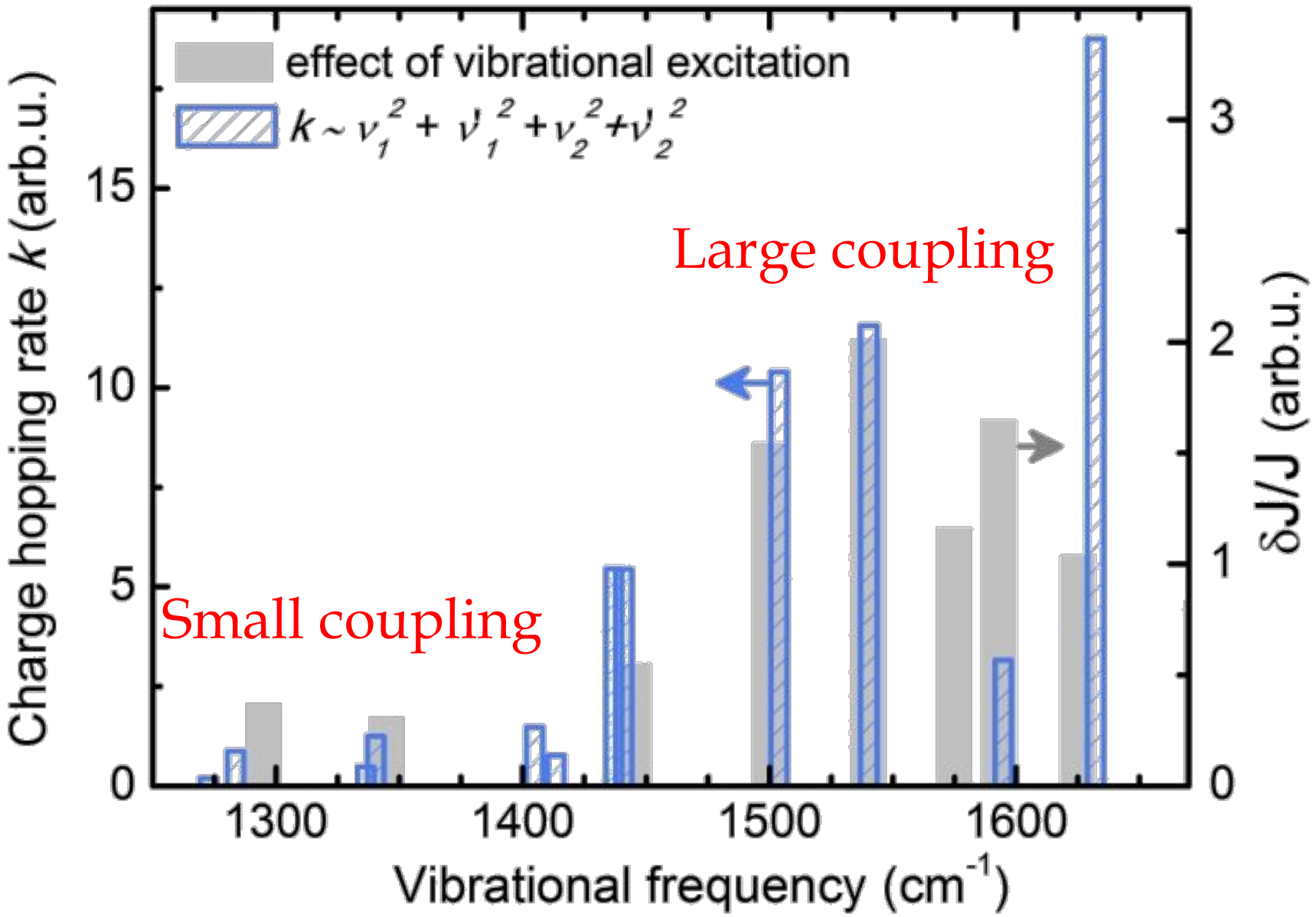
transfer integral

$v_{ij}=dt_i/dQ_j$

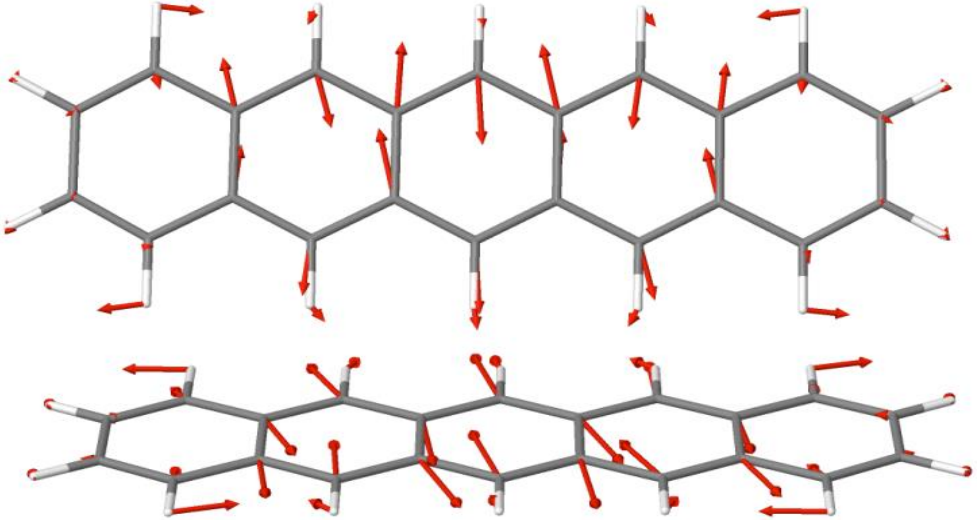
Vibrational coordinate



Theory vs. Experiment

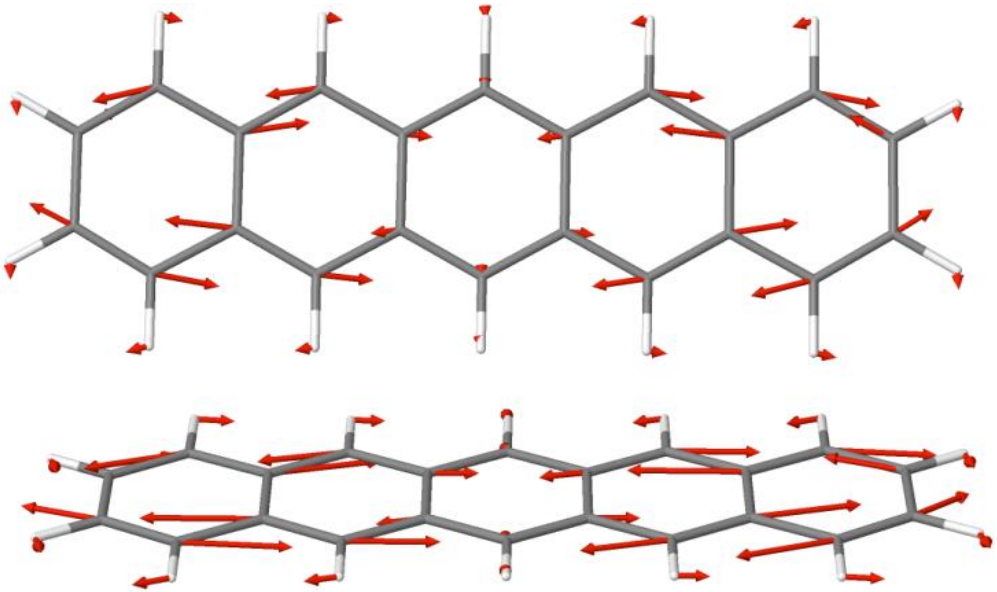


Why the effect of different modes is different?



~ 1300 cm^{-1}
Weak coupling
Vibration along
the short axis

~ 1600 cm^{-1}
Strong coupling
Vibration along
the long axis



Real time observation of organic cation rotation in $CH_3NH_3PbI_3$ perovskites

UNIVERSITY OF CAMBRIDGE

Aditya Sadhanala

FOM Institute AMOLF

Oleg Selig
Yves Rezus
Huib Bakker

cnrs dépasser les frontières

Zhuoying Chen
Zhehua Sun

UNIVERSITY OF BATH

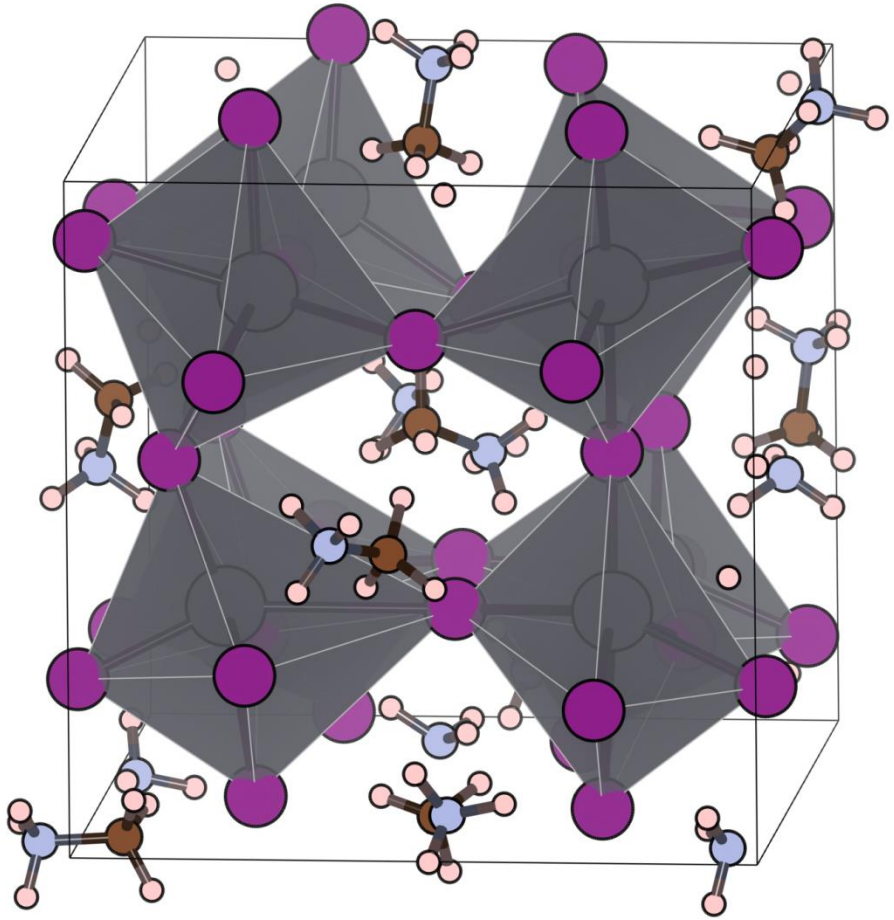
Jarvist Frost
Aron Walsh

University of Groningen Zernike Institute for Advanced Materials

Thomas Jansen

iL INNOVATION LAB thinking works

Robert Lovrincic
Christian Muller



Perovskites for solar cells

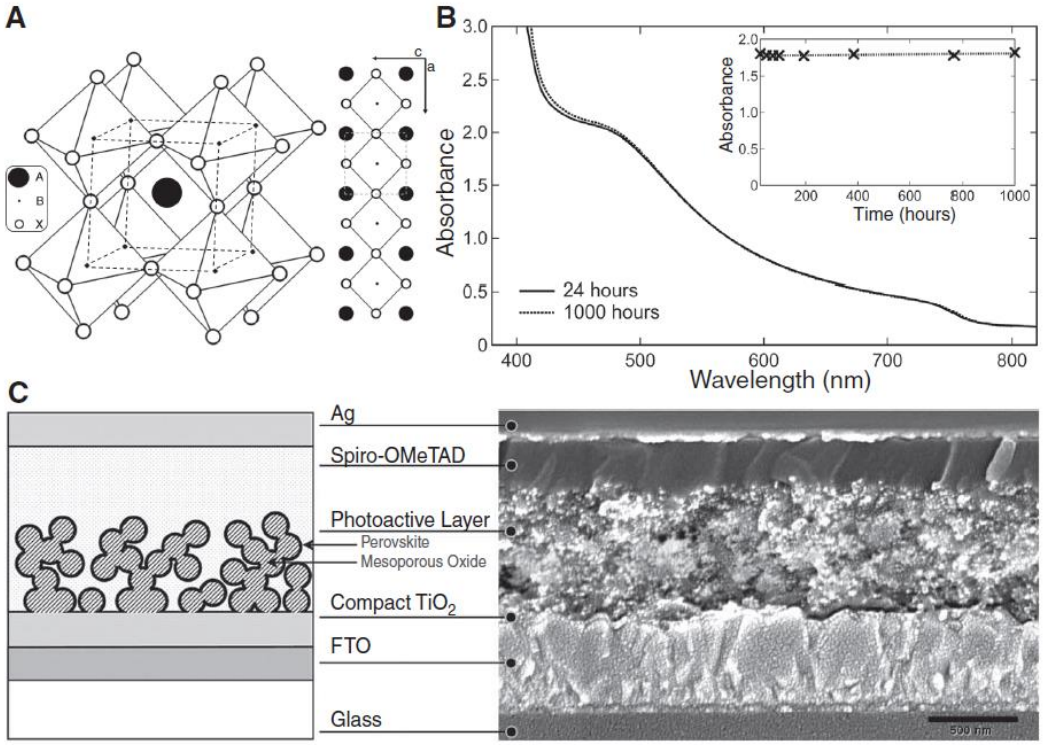
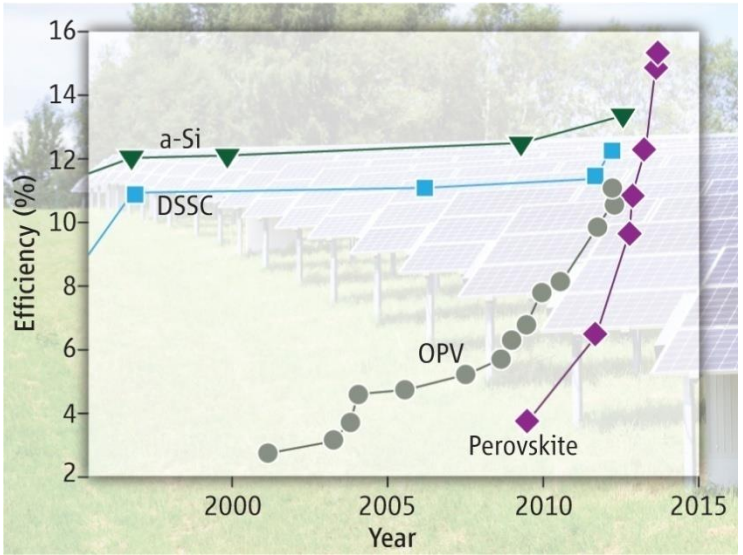


Fig. 1. (**A**) Left: Three-dimensional schematic representation of perovskite structure ABX_3 (A = CH_3NH_3, B = Pb, and X = Cl, I). Right: Two-dimensional schematic illustrating the perovskite unit cell. (**B**)

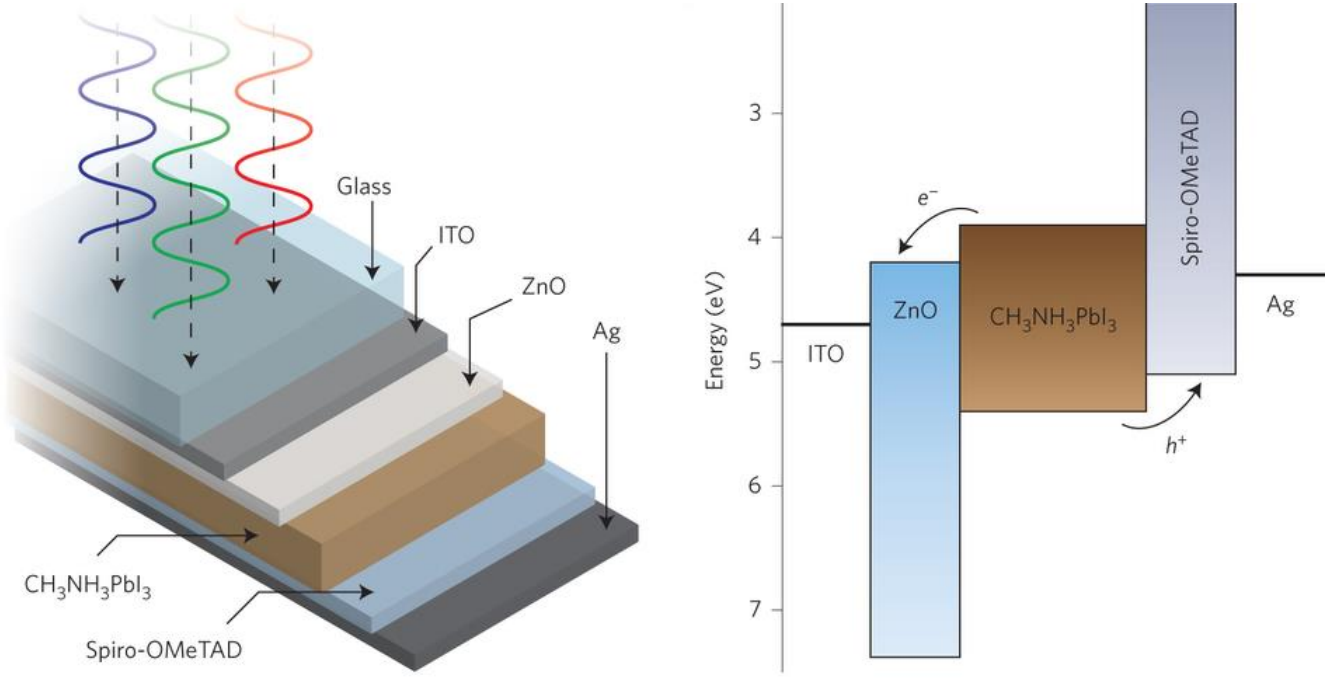
- A hybrid material
- Was developed as a dye
- Allows making solution processed thin film PVs
- Good for OLEDs/lasers



Liu el al *Science* (2012)
Kim et al *Sci Rep* (2012)

Planar perovskite solar cells

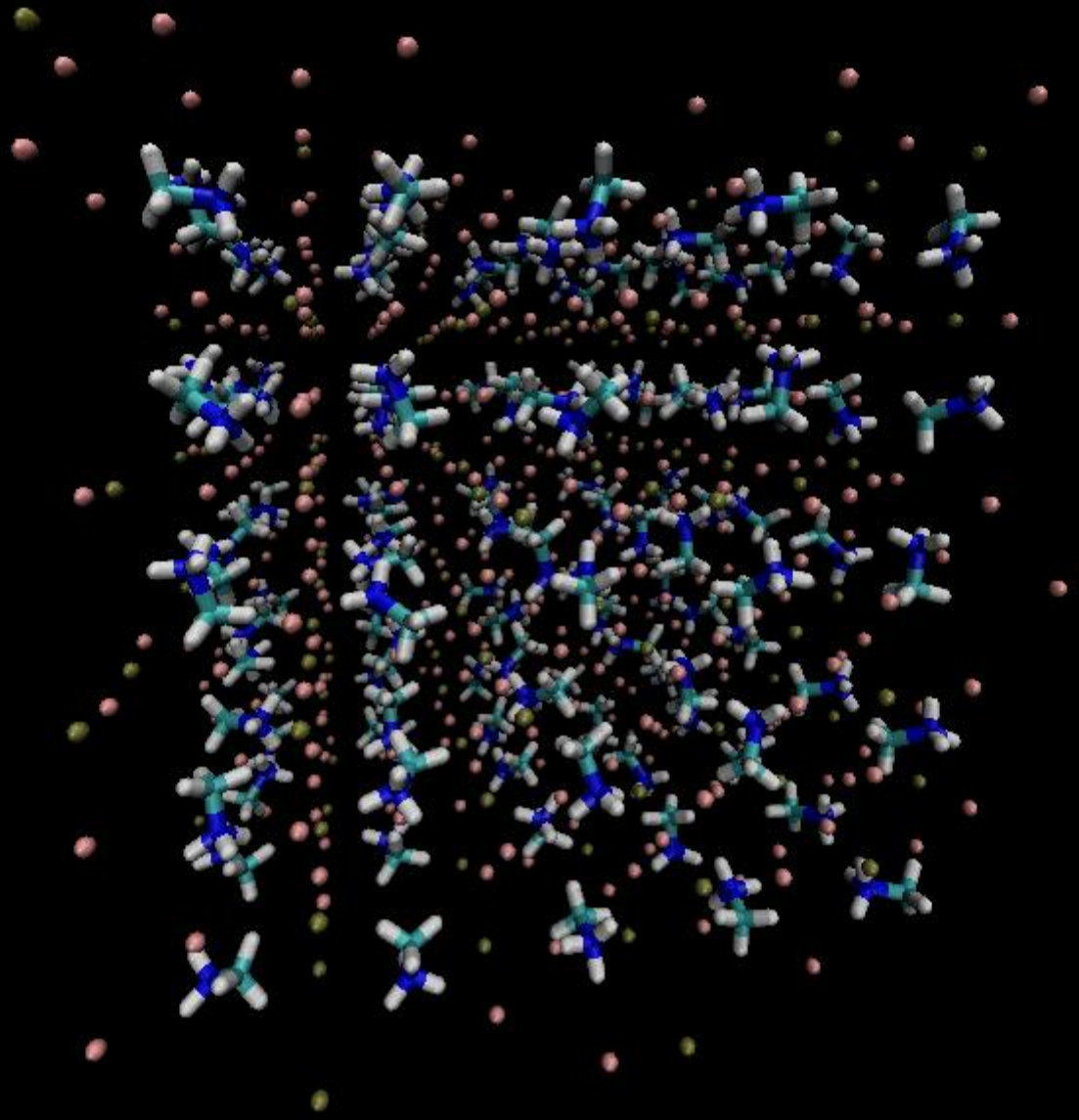
Liu et al, Nat. Photonics (2013)



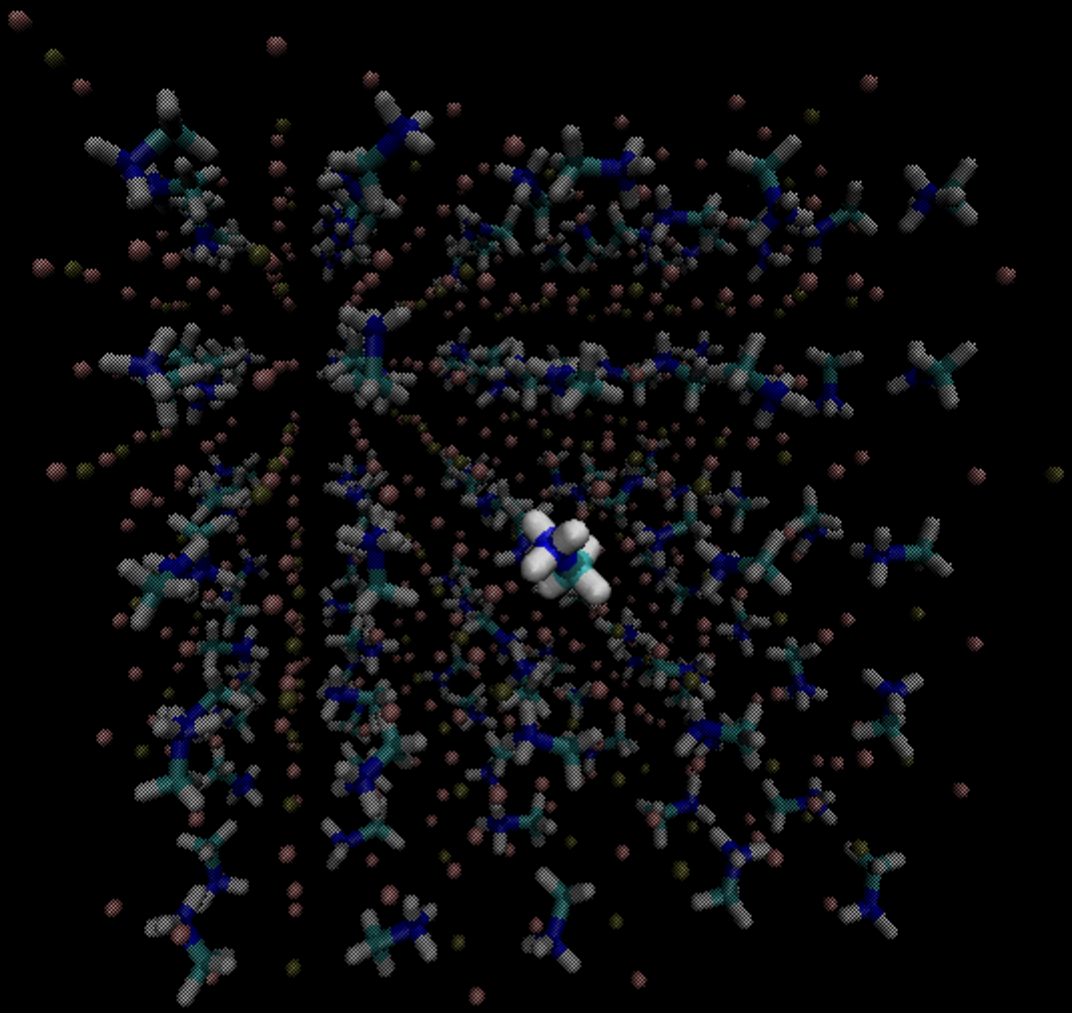
MAPbI3 perovskite as a 'solution-processible GaAs'

- Special properties due to the 'soft' character?
- 'exotic' effects like MEG or hot carriers?

Structural Dynamics:

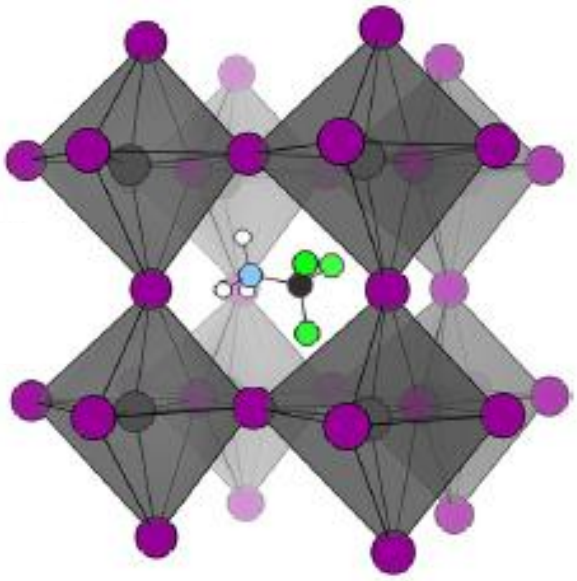


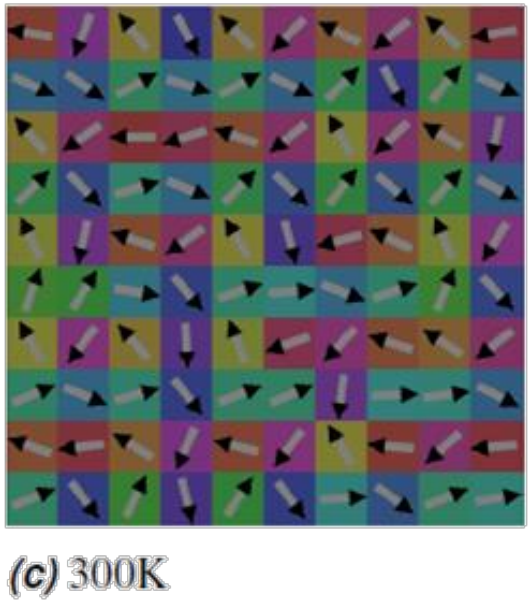
Structural Dynamics:

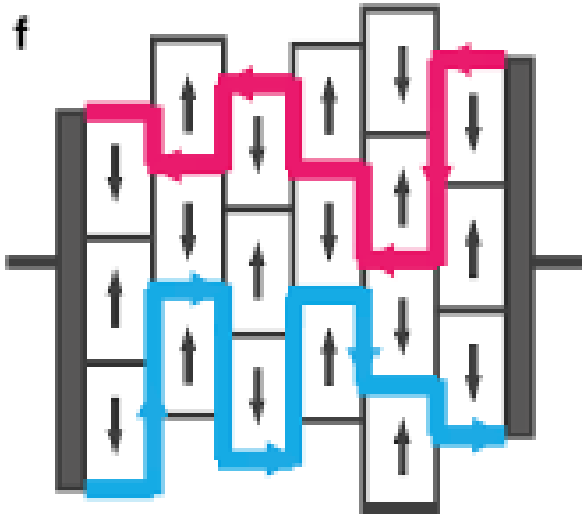


Molecular dipole effect in perovskites

Frost et al, NanoLet 2014
Forst et al, APL 2014
Stoumpos et al, InorgChem 2013







Presence of mobile dipole would imply:
- Higher dielectric constant
- Lower exciton binding energy
- Induction of additional (ferroelectric) internal field
- Segregation of charge transfer pathways

How large is CH_3NH_3 dipole mobility?

Previous knowledge

Back-of-the-envelope:

- dipole ~2 Debye
- dipole + 10^6 Vm^{-1} = 0.1meV
- dipole + dipole = 50 meV

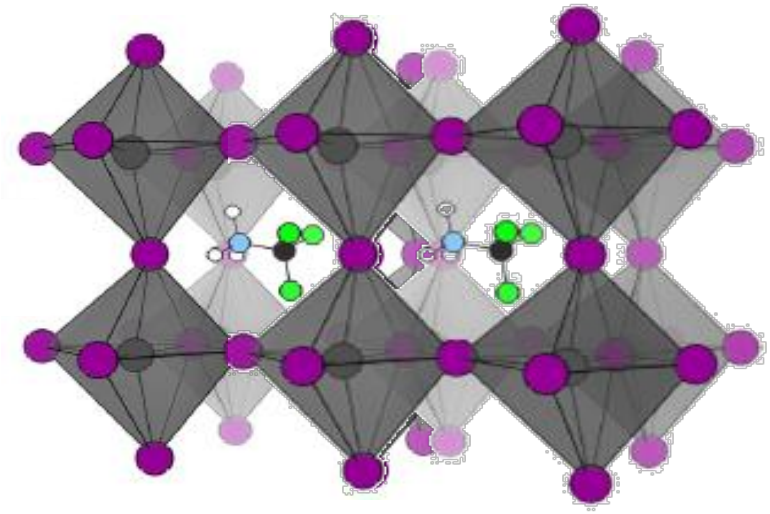


Table 1. Spin-lattice relaxation times T_1 and effective rotational correlation times τ_c for the methylammonium ion in $CH_3N(D,H)_3PbX_3$ halides at 303 K

	CL	BR	IO
$T_1(^2H)$, s	6.06	6.21	4.76
$\tau_c(^2H)$, ps*	0.364	0.355	0.463
$T_1(^{14}N)$, s	0.22	0.24	**
$\tau_c(^{14}N)$, ps*	0.25	0.23	**

NMR:

~ 0.25-0.4 ps

Wasylishen et al, Solid State Com. 1985

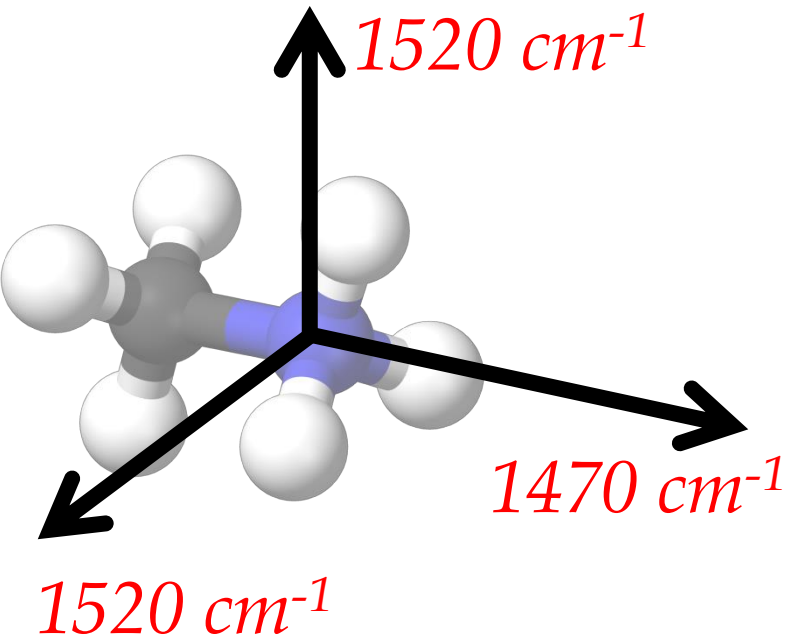
MD simulations: ~5ps

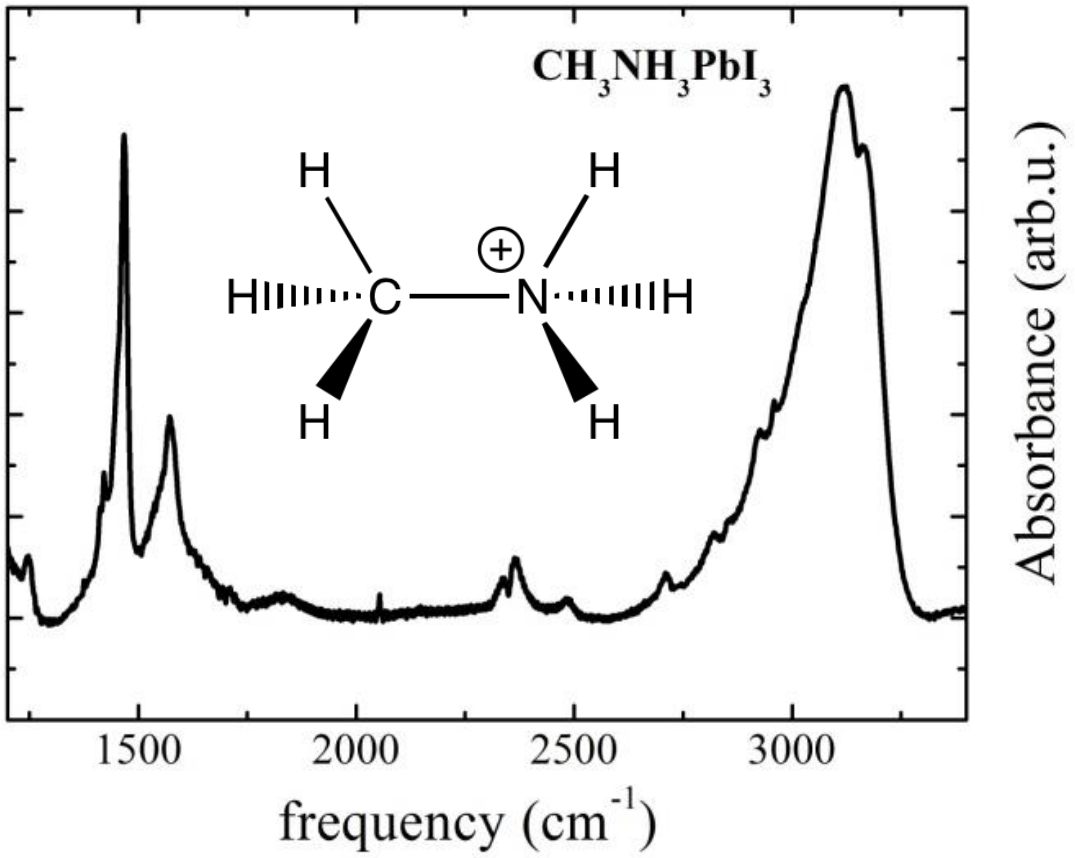
Mosconi et al. PCCP 2014

Angelis et al. Chem Mat. 2014

pointed out in ref. 15. During the simulation, the MA cations accomplish at least one rotation along one of the reference axes (see Tables SI1 and SI2, ESI†), providing a mean rotation time of the order of a few ps (5.47 ps at 268 K, 4.52 at 319 K).‡ These results agree quite well with the experimental estimation of the C–N rotational correlation time in $MAPbI_3$ of 0.46 ps[14] and with the

Vibration as a probe for dipole orientation



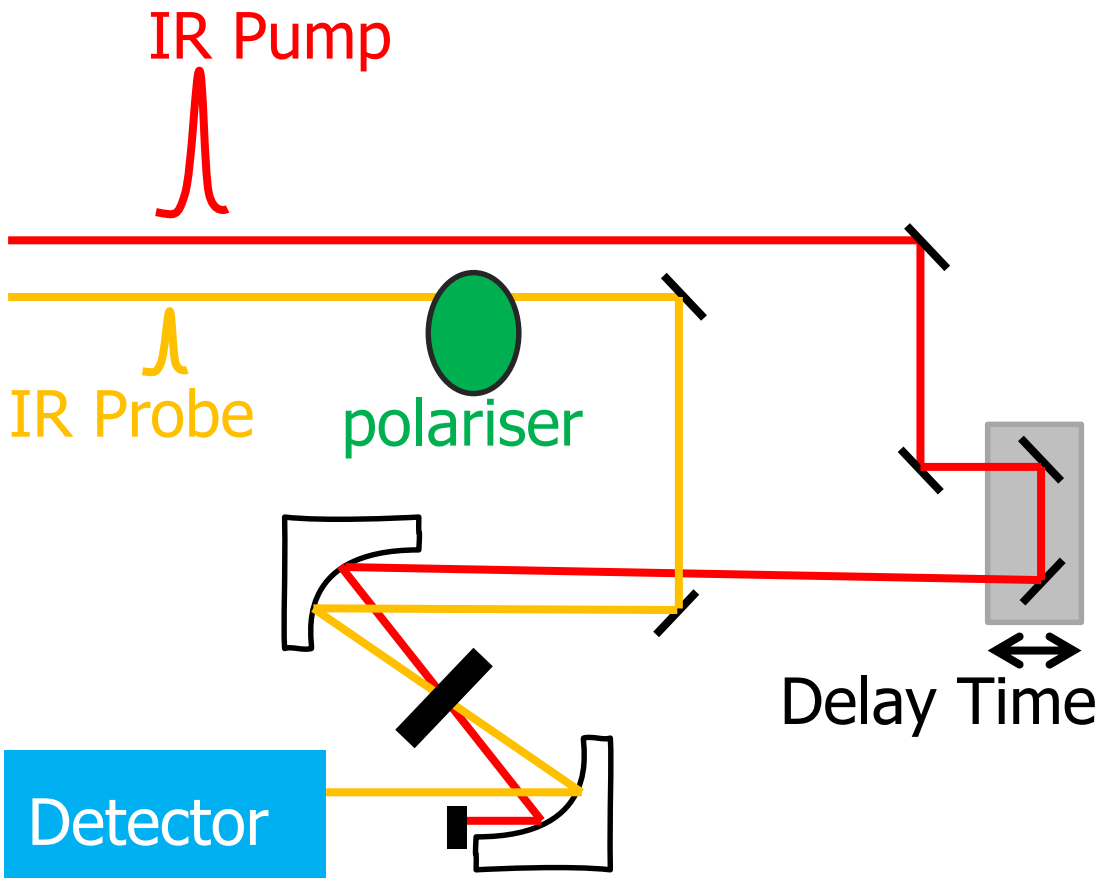


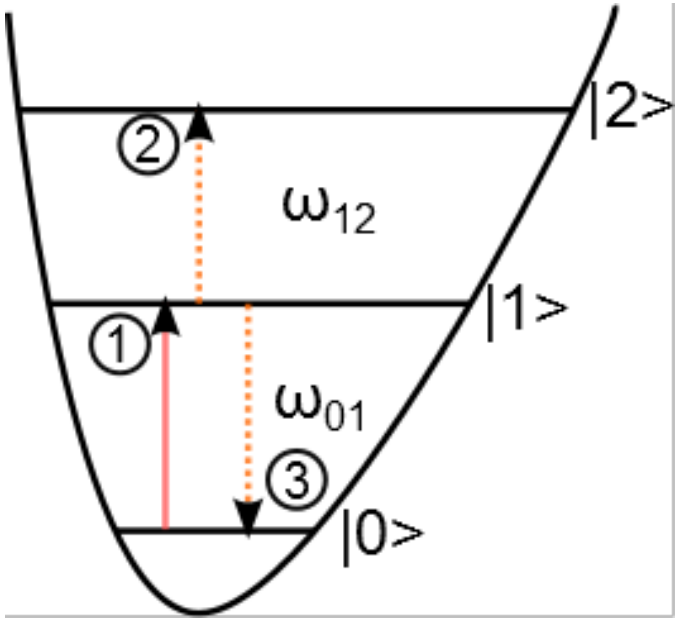
- 1470 cm^{-1} vibration is aligned with molecular dipole

- It is a probe for dipole orientation

Vibrational pump probe spectroscopy

- CH bending – anharmonic oscillator
- predictable pump-probe response

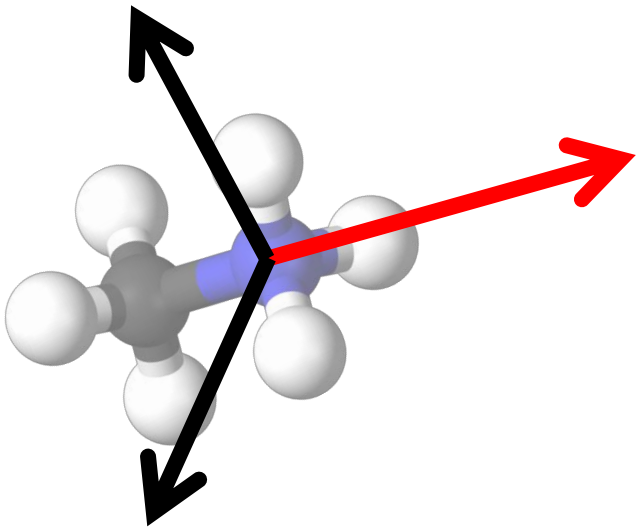


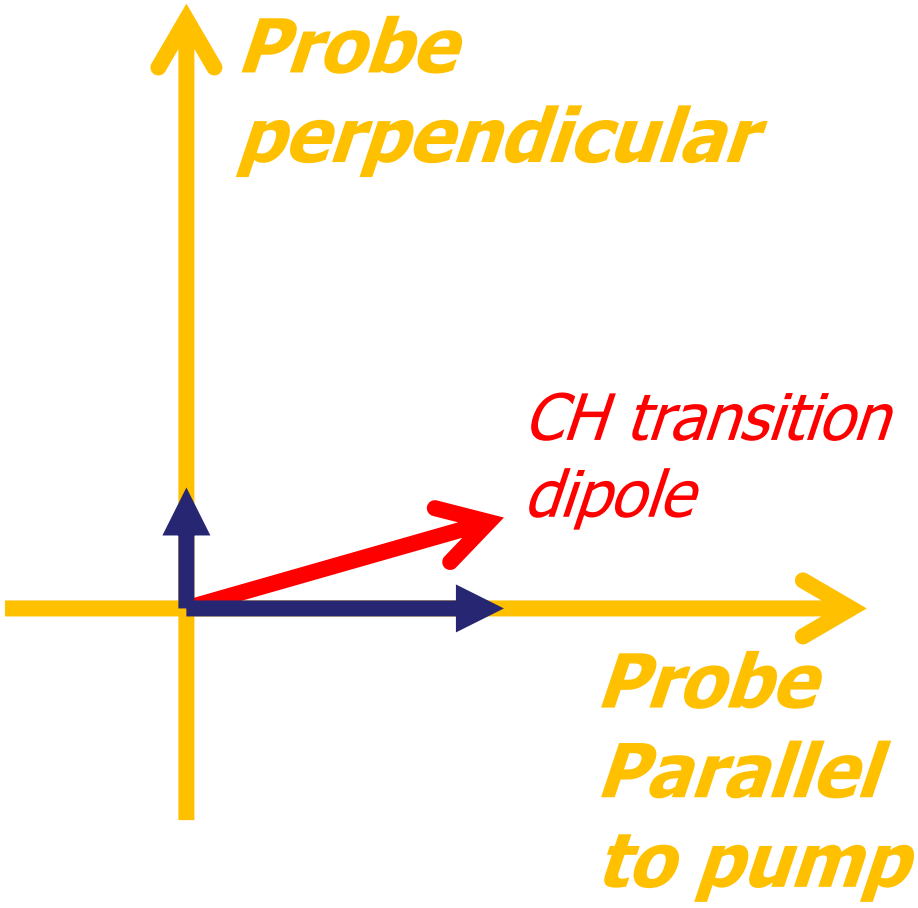


By Oleg Selig and Yves Rezus @ AMOLF

Vibration as a probe for dipole orientation

Pump-probe at sort delay times

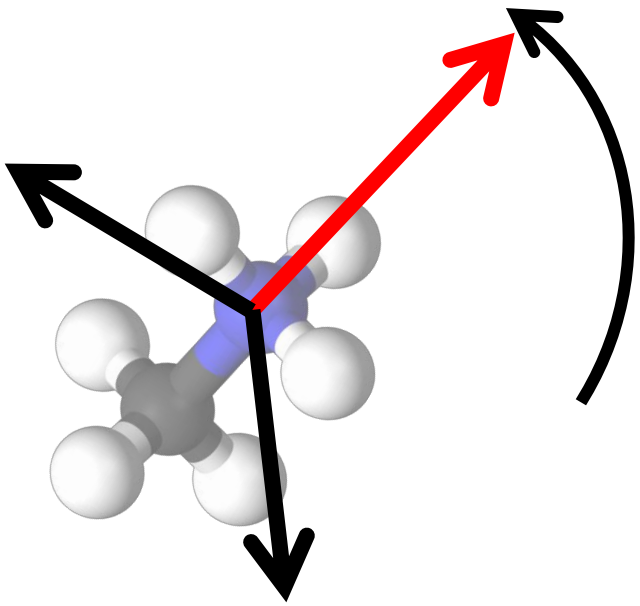


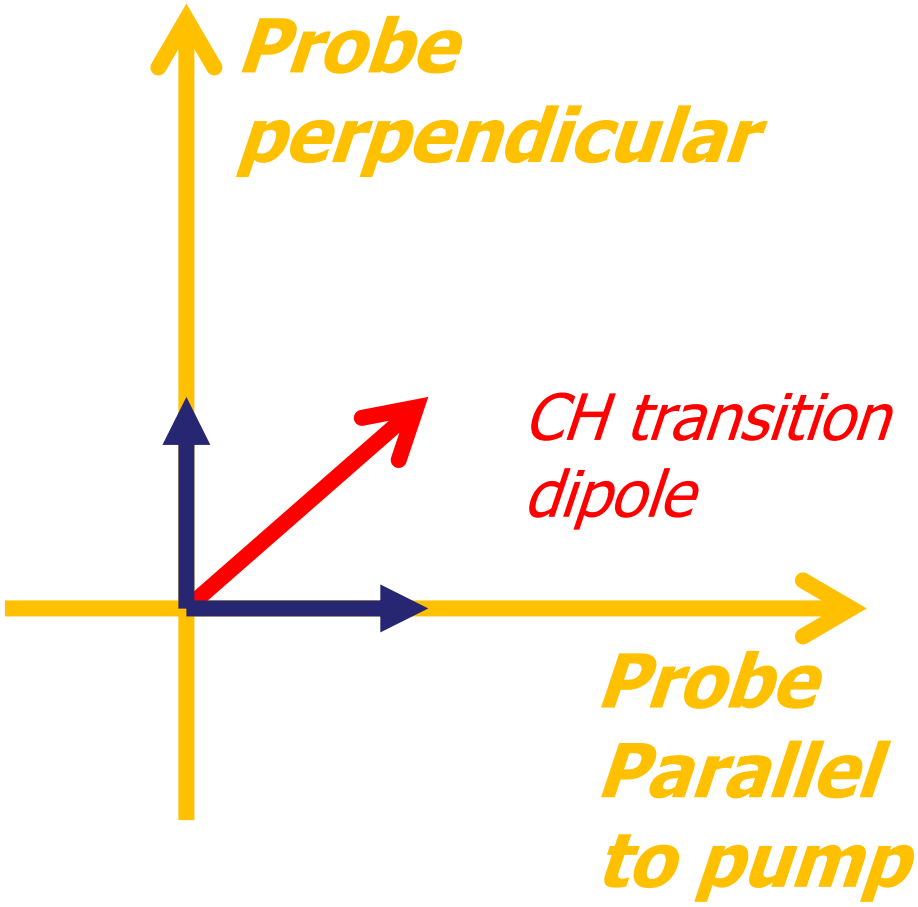


Ratio between signals in parallel and perpendicular channels reflect the orientational dynamics

Vibration as a probe for dipole orientation

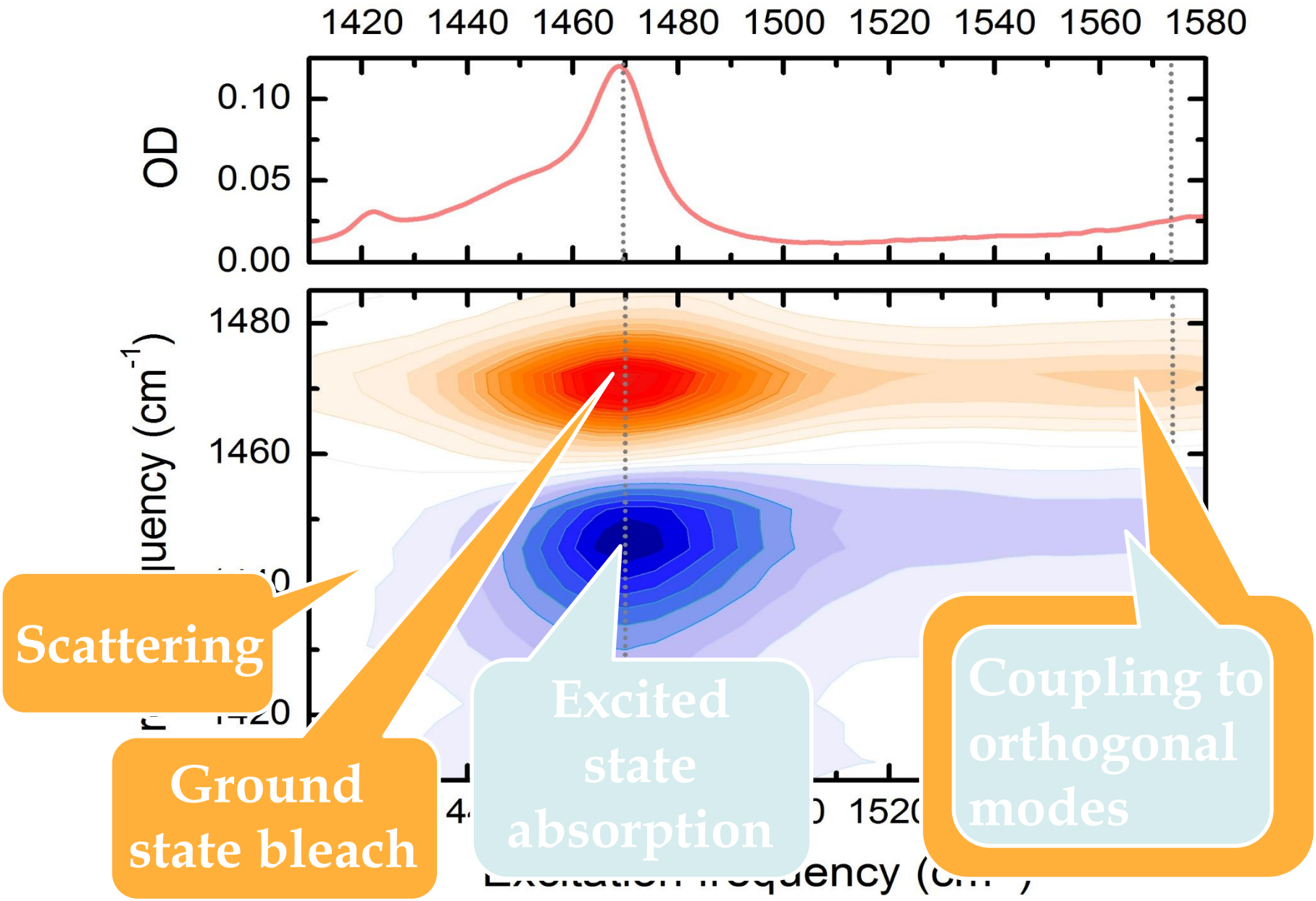
Pump-probe at
long delay times



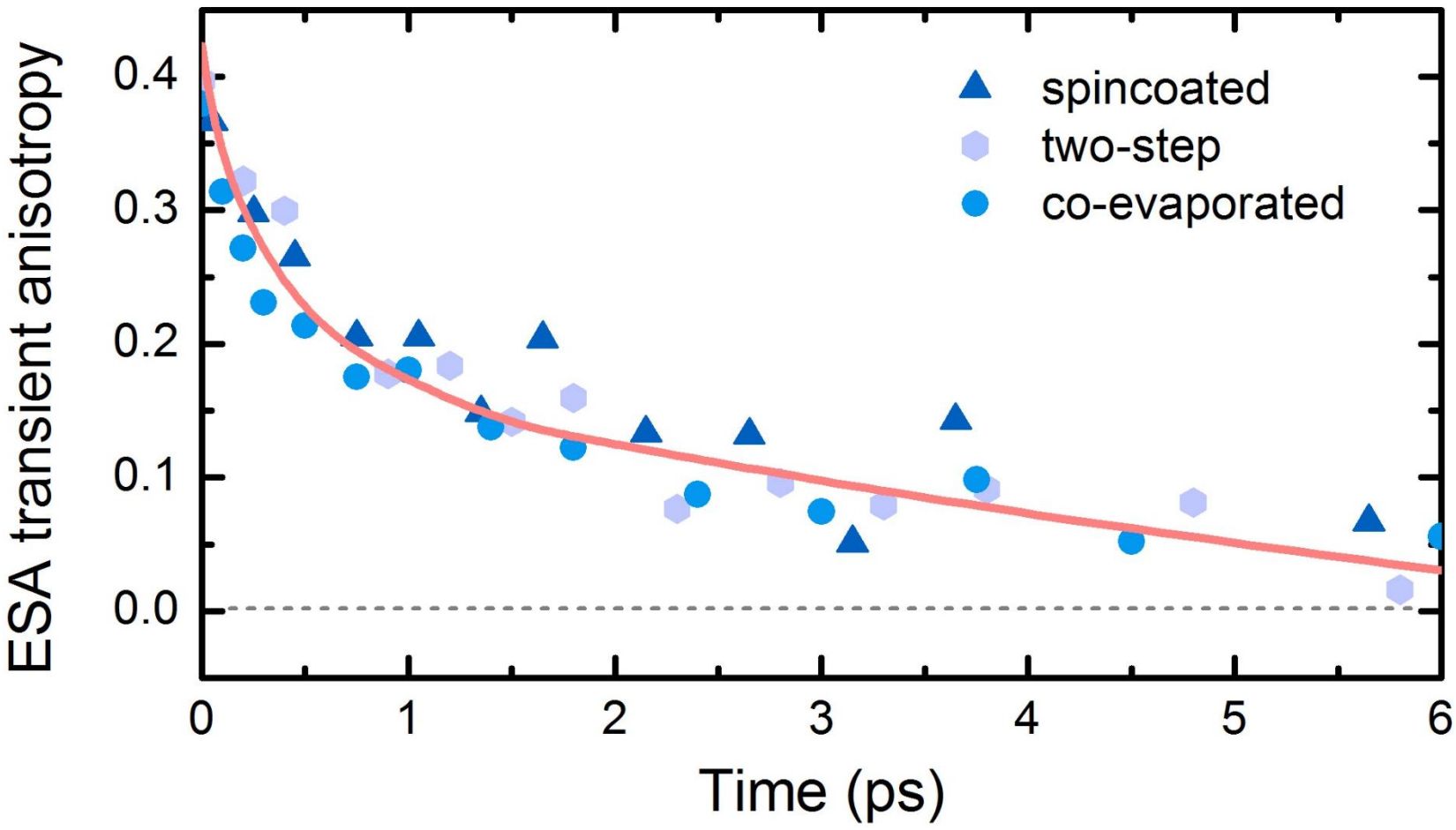


Ratio between signals in parallel and perpendicular channels reflect the orientational dynamics

2D photon echo measurements

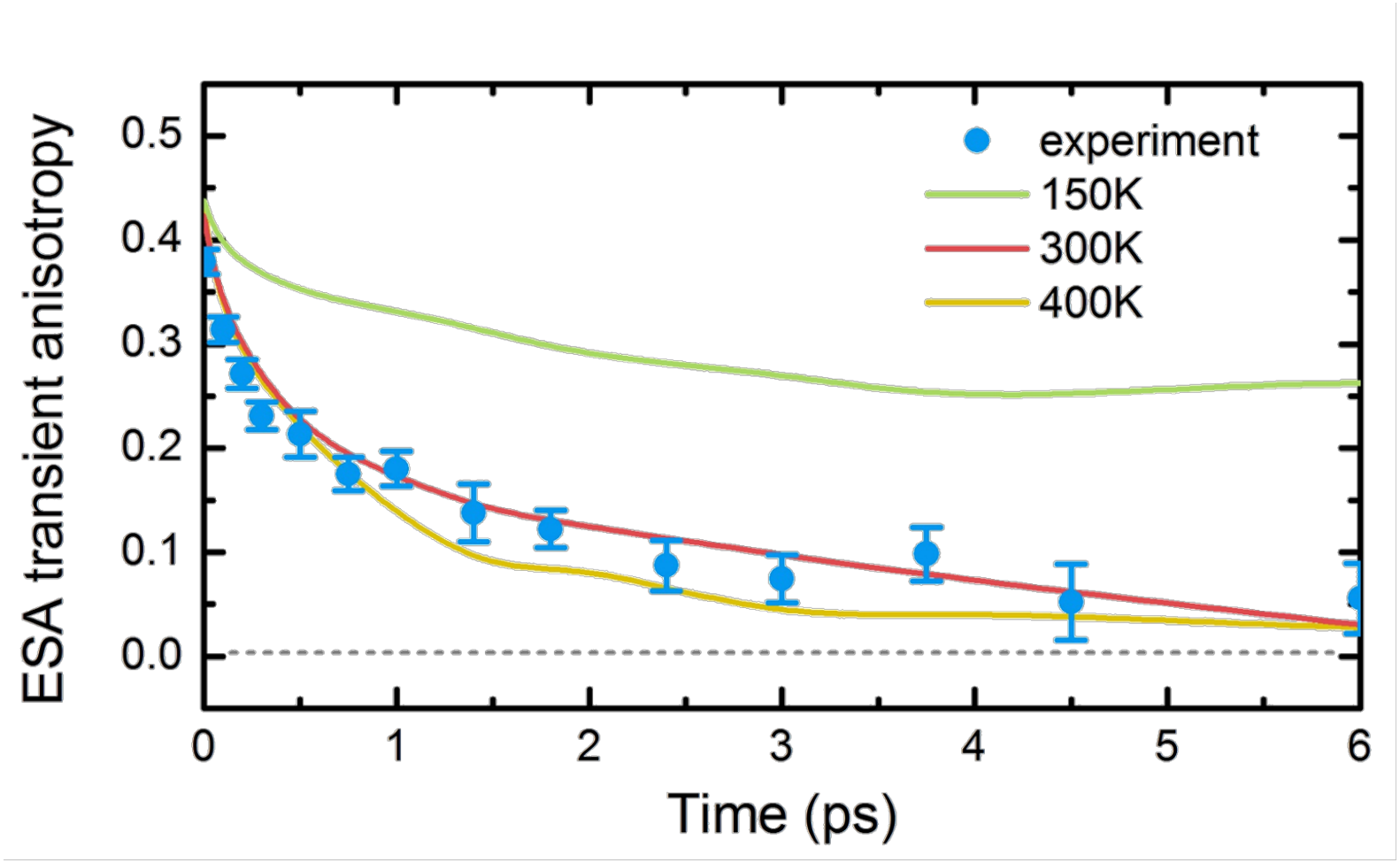


Anisotropy dynamics of MA in perovskites



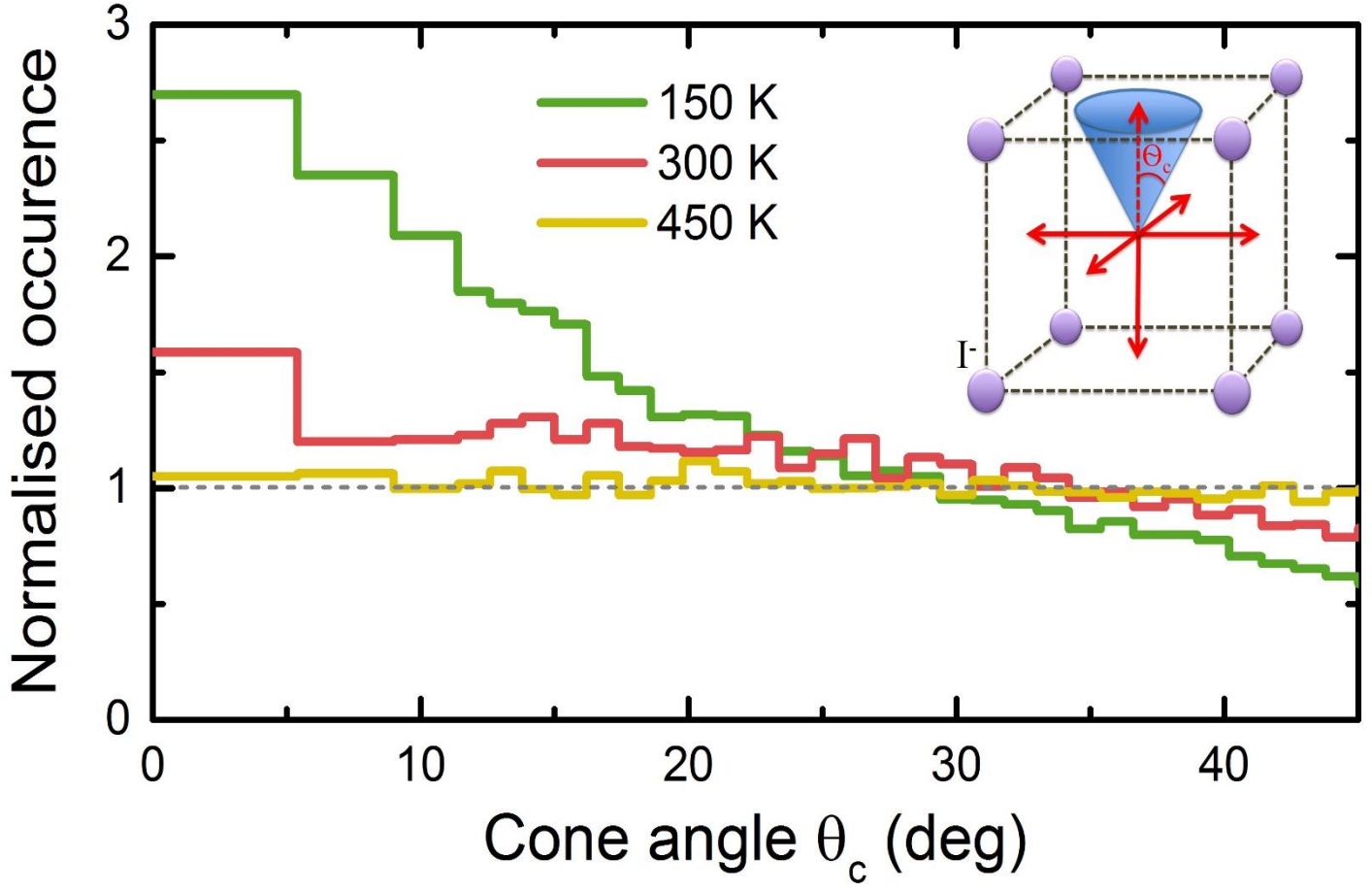
- Dynamics independent on the film preparation
- Bimodal behaviour – two different motions
- Red line – calculations based on *ab initio* MD by Jarvist Frost

Theory vs. Experiment: anisotropy dynamics



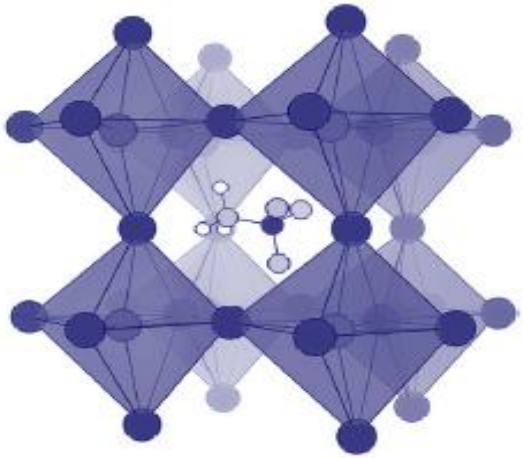
- Very good agreement experiment vs. theory – MD confirmed
- Predicted temperature dependence
- At low temperatures one type of motion suppressed

Wobbling-in-cone motion



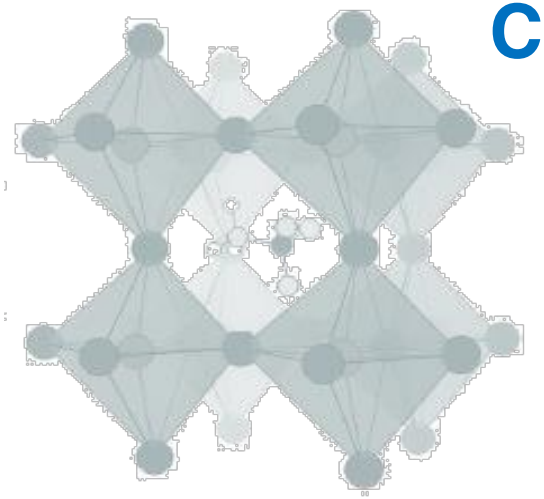
- predominant orientation of MA in the lattice
- librations (0.4ps) + jumps (2ps)

$CH_3NH_3PbBr_3$, $CH_3NH_3PbCl_3$ perovskites

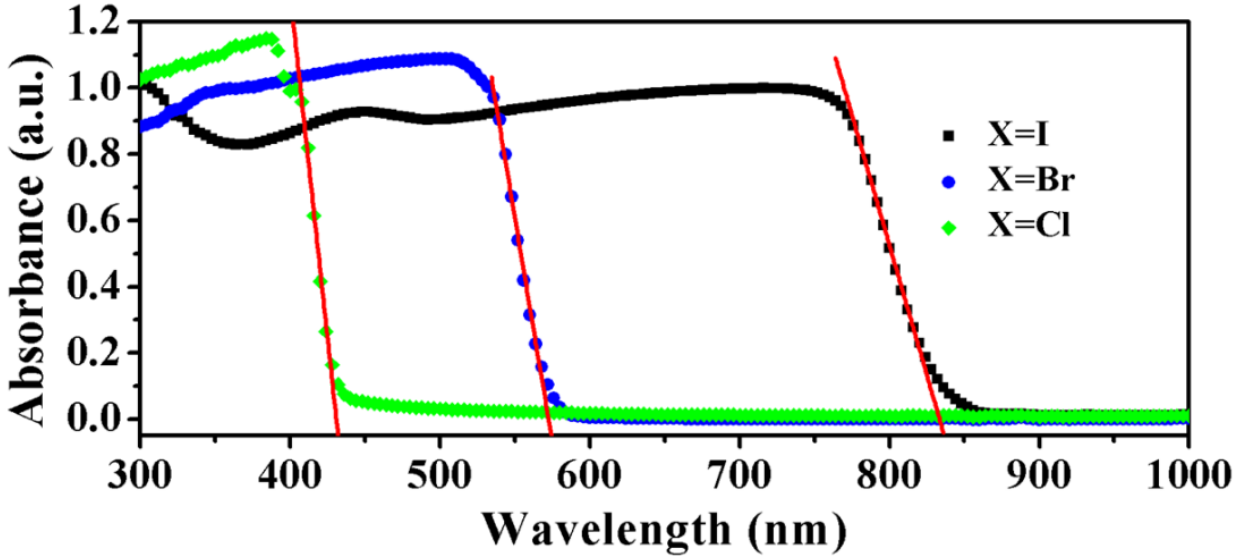


Br

- Br, Cl - is less polarisable
- Lattice period is ~ 5% smaller
- Tuning the bandgap

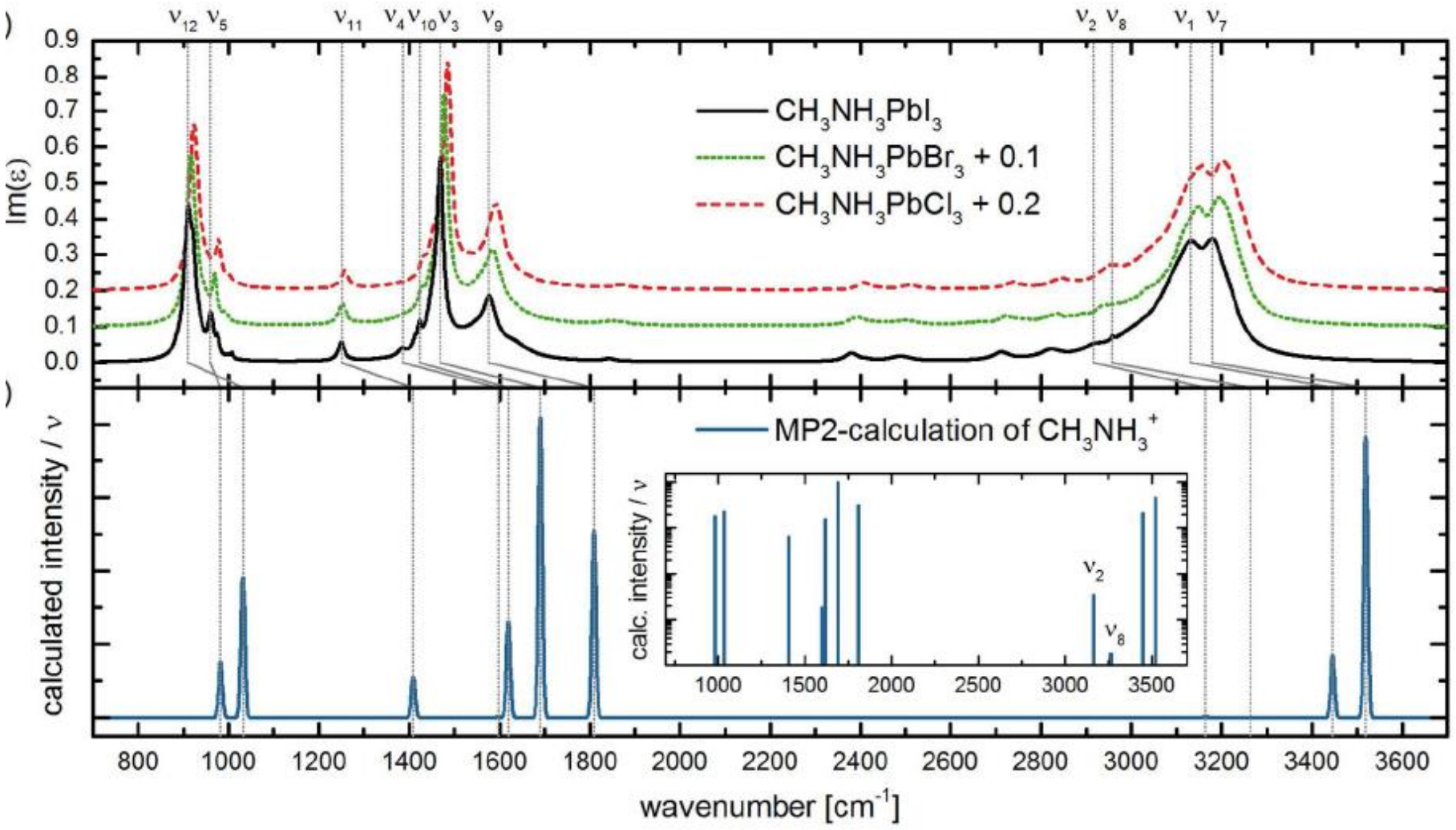


Cl



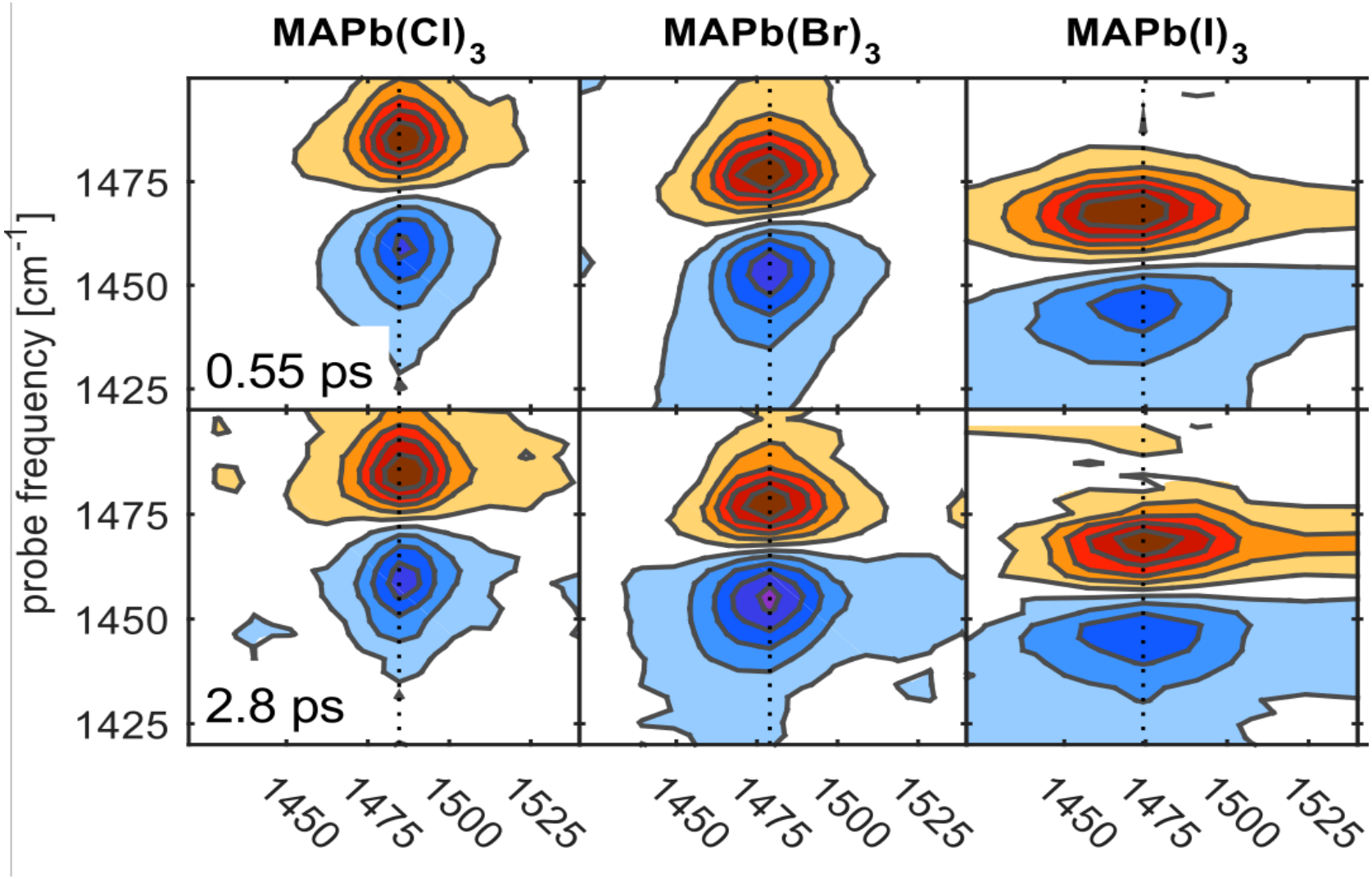
Su, Mat Views 2015

$CH_3NH_3PbBr_3$, $CH_3NH_3PbCl_3$ IR absorption



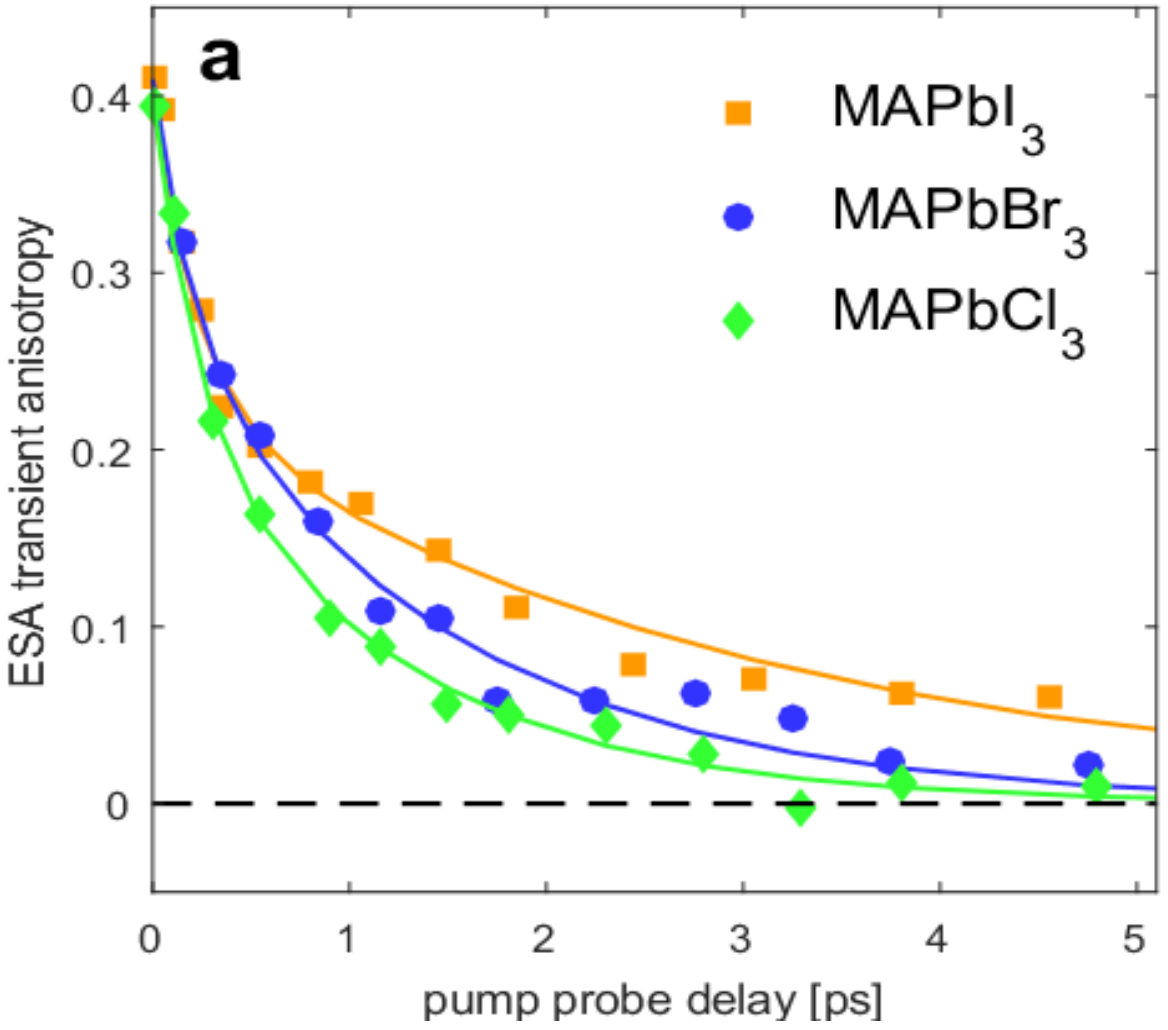
Shift of vibational modes due to the change in led halide lattice

$CH_3NH_3PbBr_3$, $CH_3NH_3PbCl_3$ 2DIR



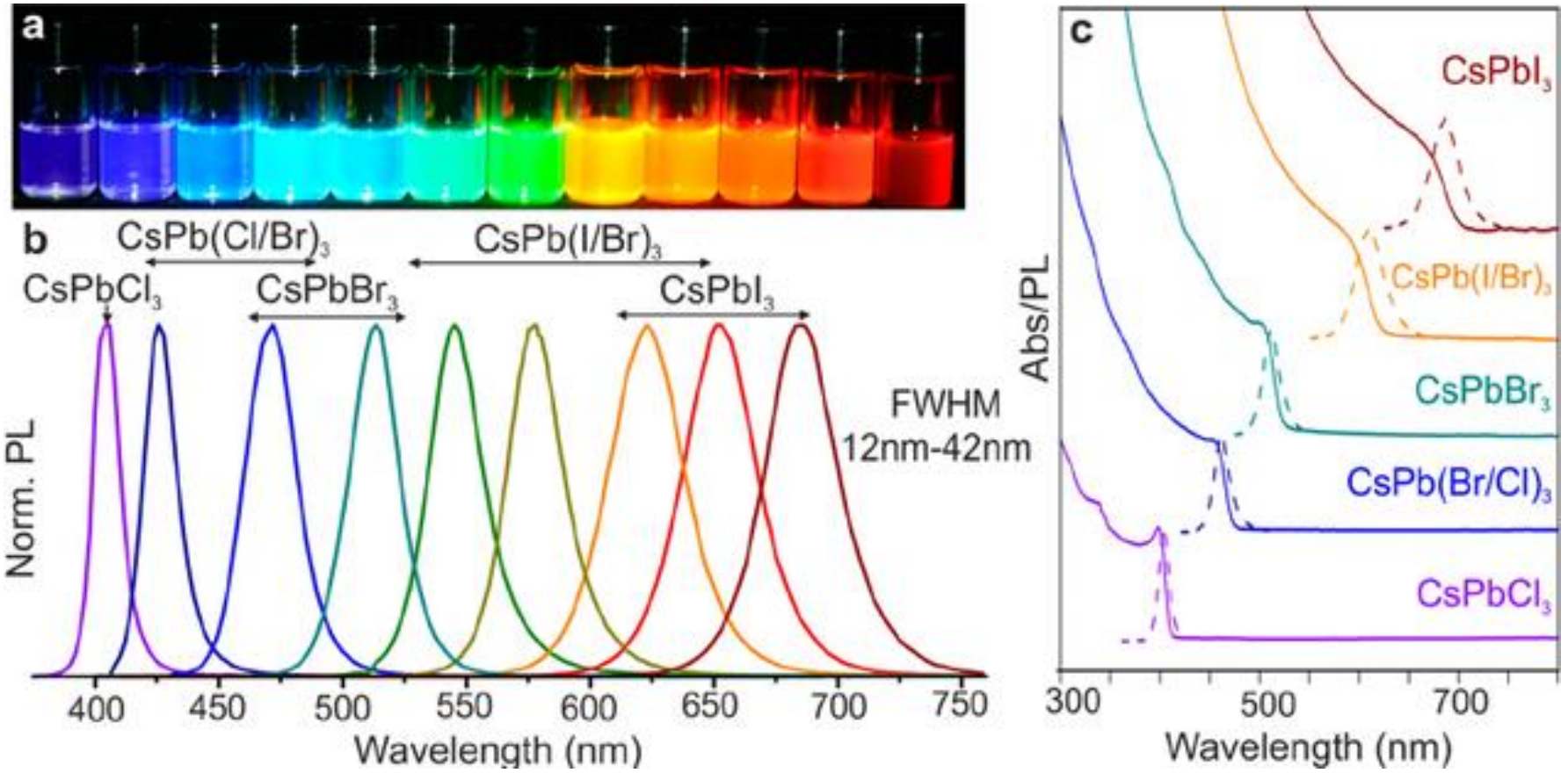
Shift of vibational modes due to the change in led halide lattice

Different halides – cation rotation



- The smaller is the unit cell the faster is reorientation
- Wobbling motion is the same, but jumping rate changes
- Polarisability is more important to than the hindrance in space

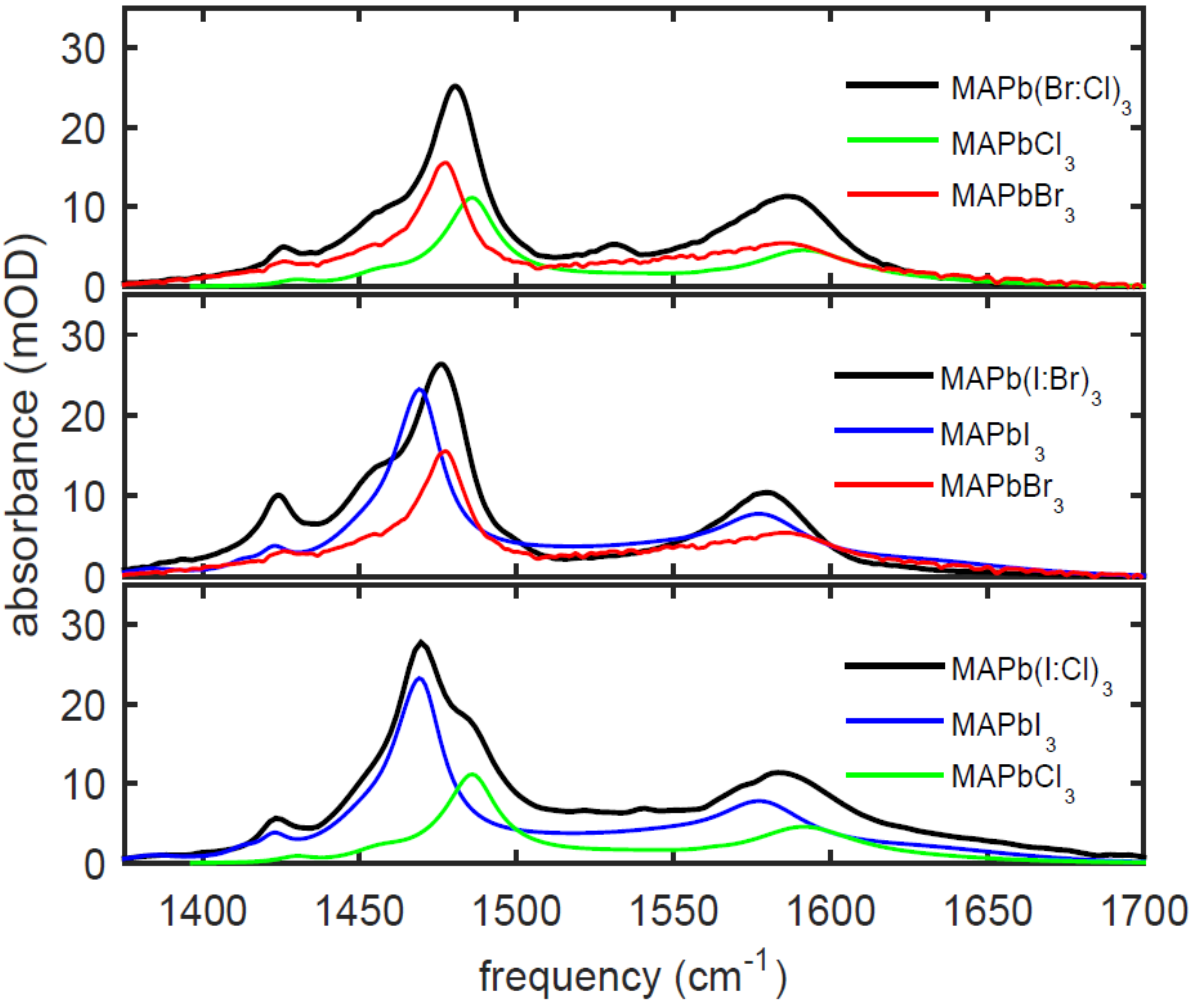
Mixed-halide perovskites MAPb $(A_xB_{1-x})_3$



- Statistical mixture of halide ions
- Bandgap is very tunable
- Great for LED applications

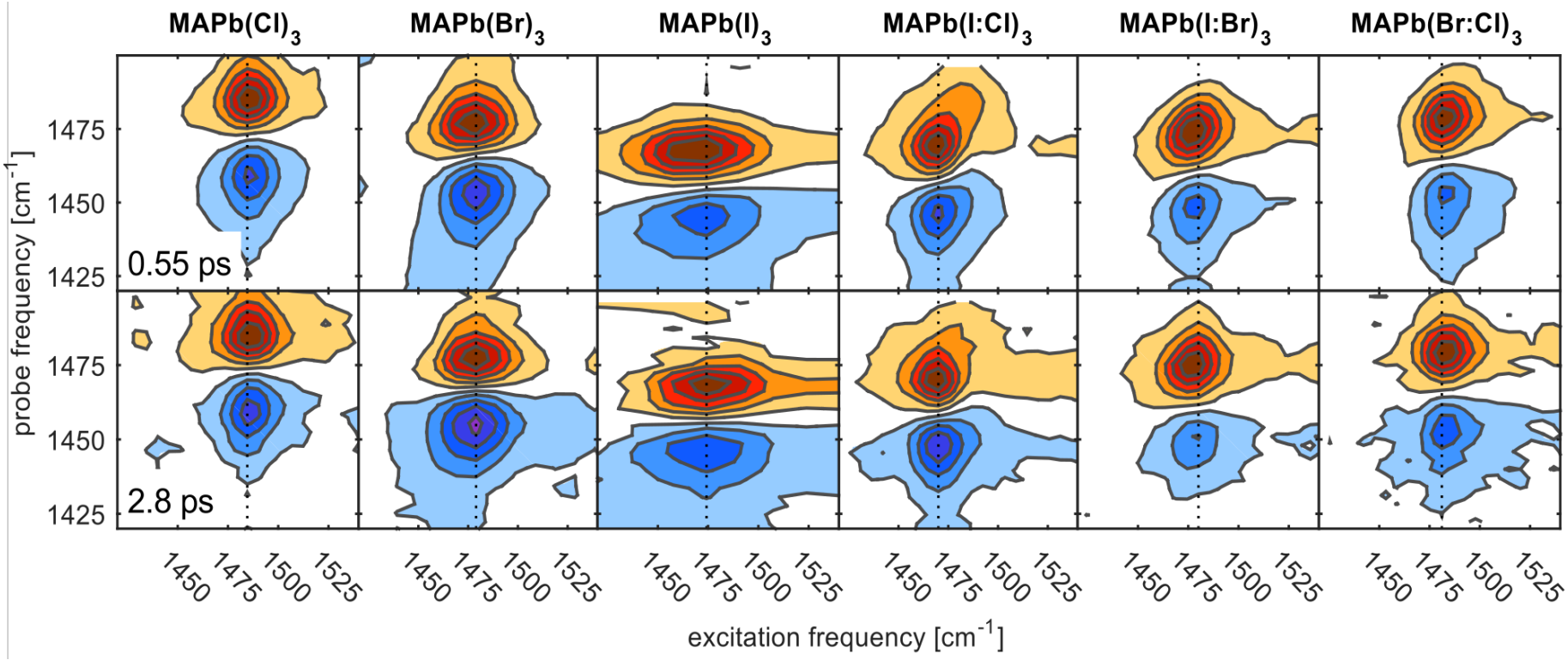
Protesescu et al NanoLett 2015

Mixed-halide perovskites IR



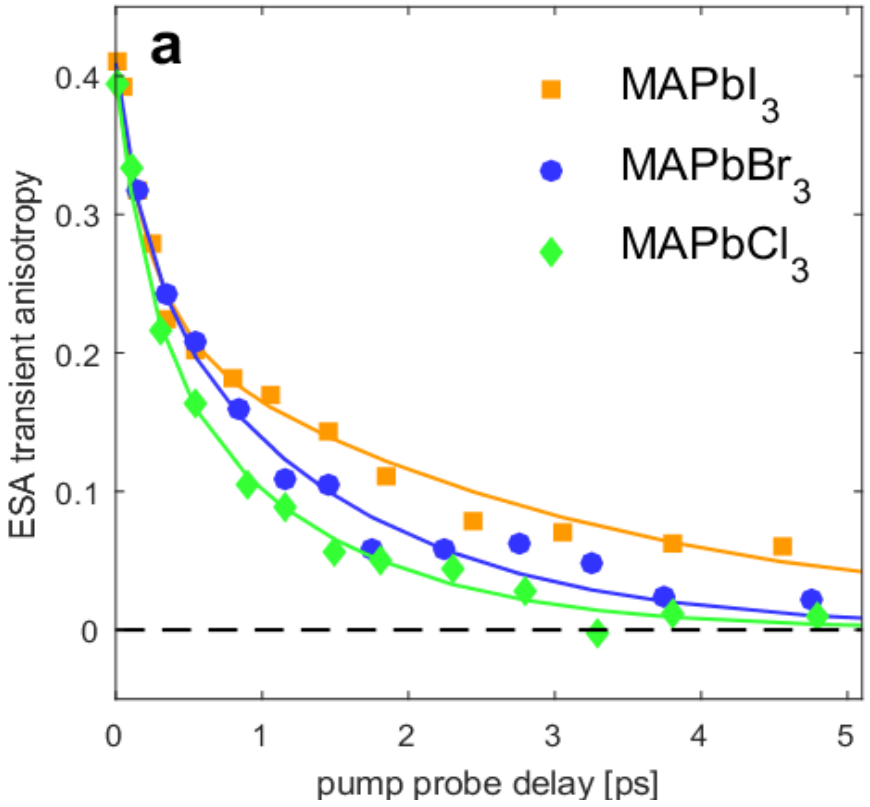
- I-Cl phase segregates
- I-Br and Br-Cl form good mixtures - alloys

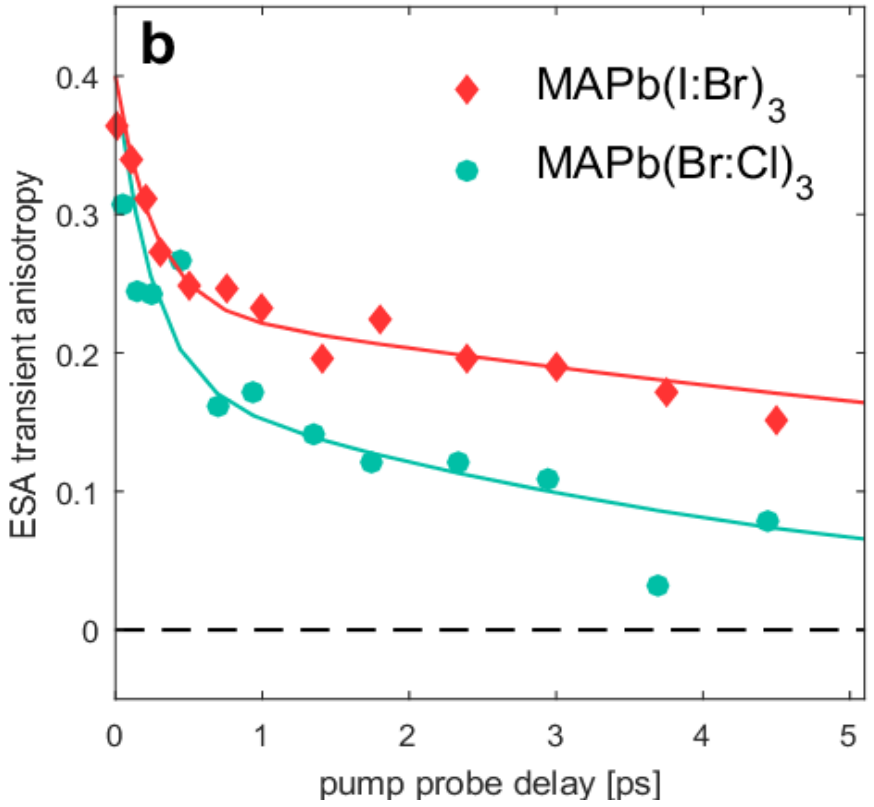
Mixed-halide perovskites 2DIR



- I:Cl confirms phase segregation… no coupling between phases
- I:Br and Br:Cl are alloys… with a slight inhomogeneity

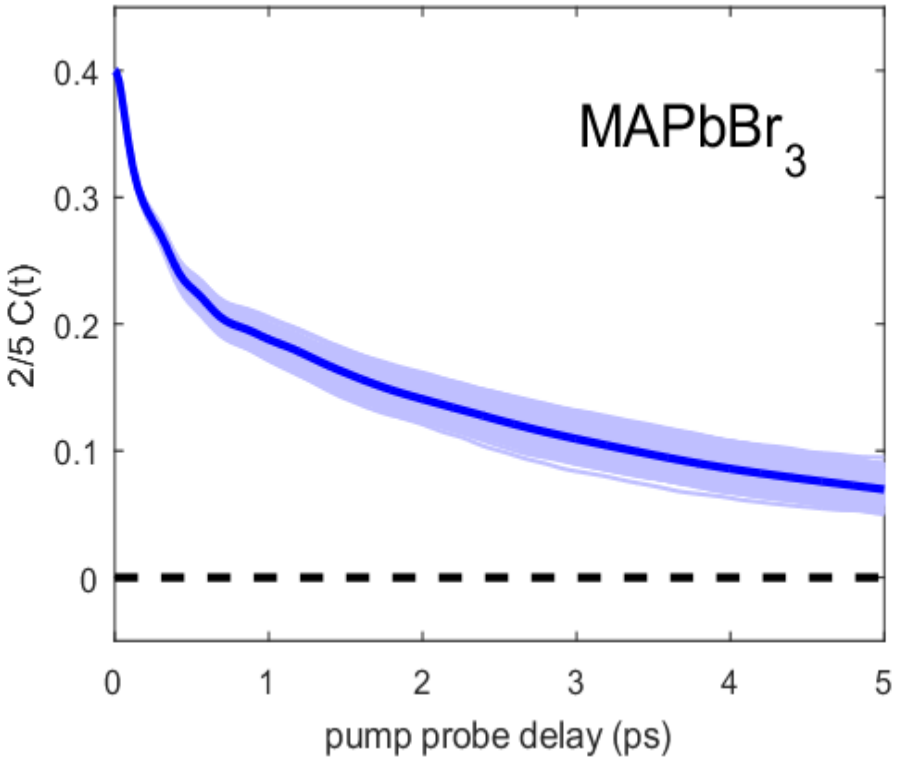
Mixed-halide perovskites – cation rotation

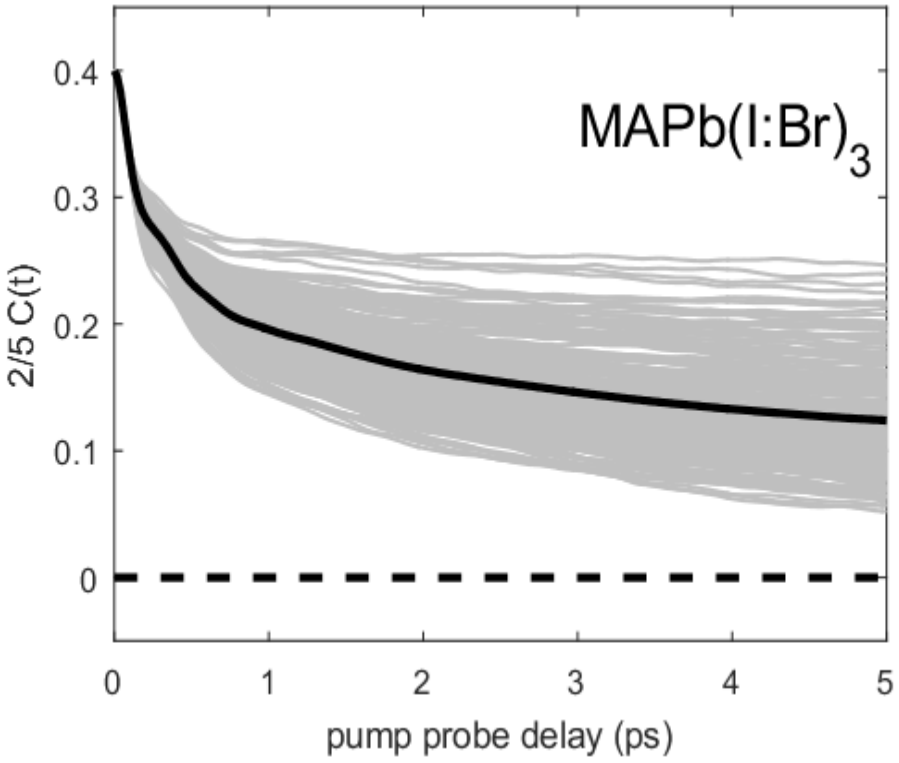




- fast component (wobbling) is not affected
- slow component is 'frozen' – MA rotation is compromised

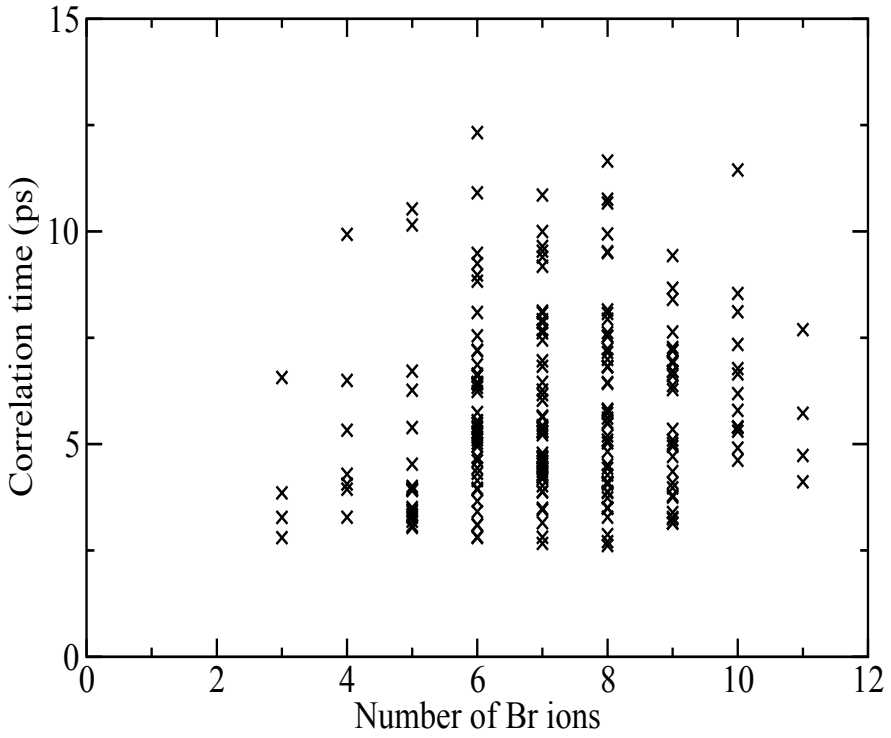
MD simulations – different MA behaviour

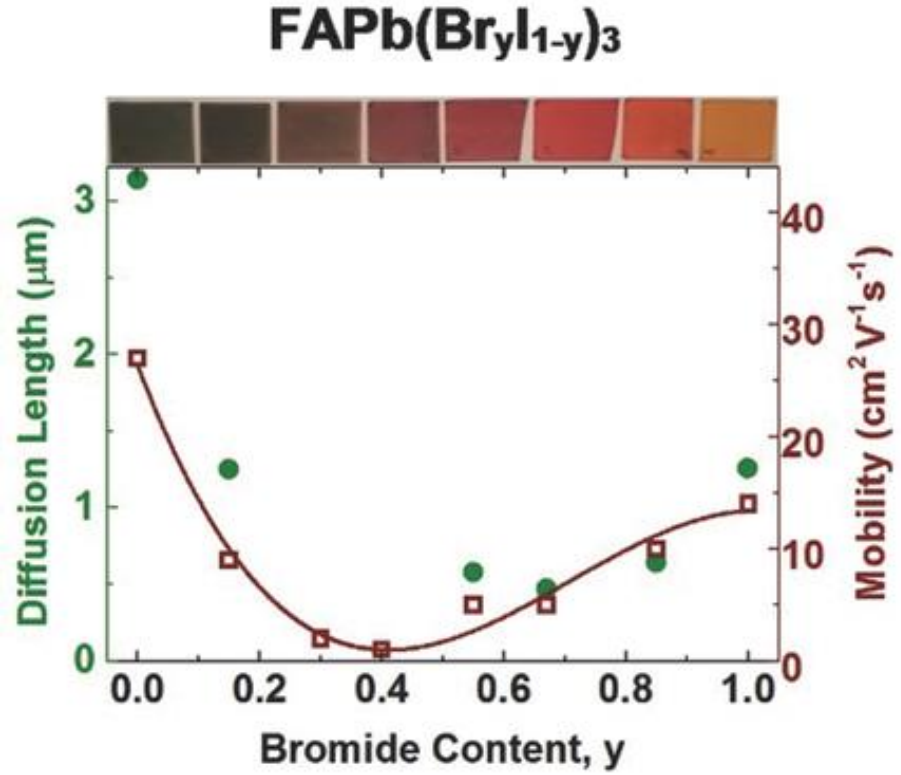




- pure halides – all cations are the same
- mixed halides – some are free and some are frozen

MD simulations – different MA behaviour





Rehman et al, Adv Mat (2015)

- Its very hard to quantify but distribution correlates with particular halide distribution in the unit cell

Conclusions

- Two-step cation dynamics in perovskites:
  - dynamic disorder is smaller
  - static disorder is larger

JPCLett.(2015), JACS (2017)

- Proof-of-principle demonstration of optical vibronic control of molecular nanodevices

Nature Comm. (2015)

- Vibrations can serve to connect electronic states and accelerate charge and energy transfer

Nature Chem. (2016)

NWO

THE ROYAL SOCIETY

erc

Why do we see dark state?

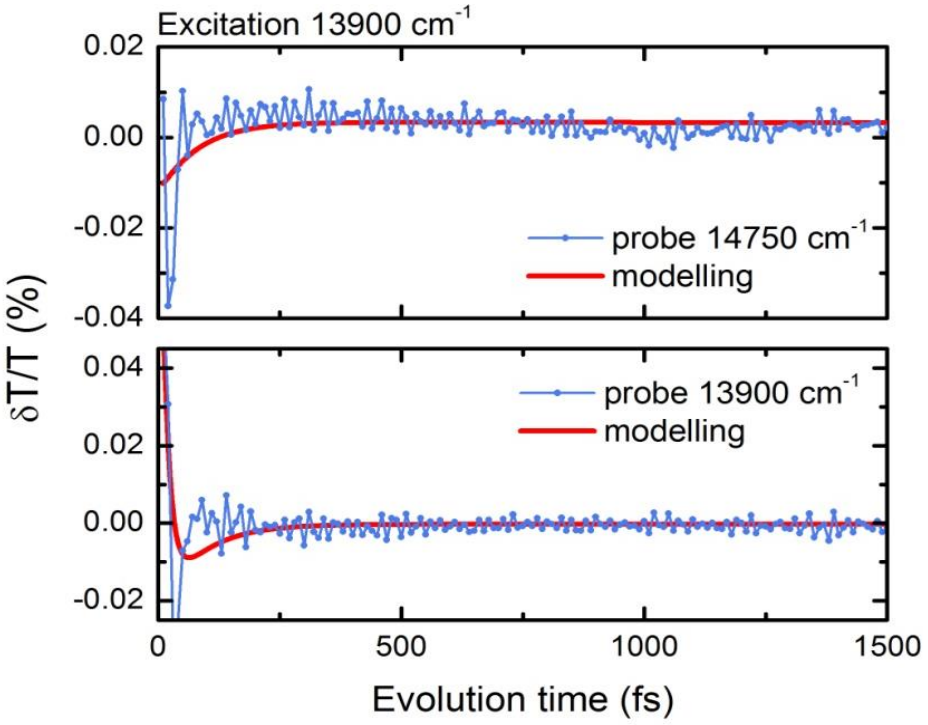
$$\mathrm{DP}^{\mathrm{SE}}_{\mathrm{reph}}/\mathrm{CP}^{\mathrm{SE}}_{\mathrm{reph}}\left(\omega_\tau=\omega_{e0},\omega_t=\omega_{e'g}\right)\sim\mu_{0e}\mu_{eg}\mu_{ge'}\mu_{e'0}e^{i\omega_{ee'}T},$$

$$\mathrm{DP}^{\mathrm{GSB}}_{\mathrm{reph}}/\mathrm{CP}^{\mathrm{GSB}}_{\mathrm{reph}}\left(\omega_\tau=\omega_{e0},\omega_t=\omega_{e'g}\right)\sim\mu_{0e}\mu_{eg}\mu_{ge'}\mu_{e'0}e^{i\omega_{g0}T},$$

$$\mathrm{DP}^{\mathrm{SE}}_{\mathrm{nonreph}}/\mathrm{CP}^{\mathrm{SE}}_{\mathrm{nonreph}}\left(\omega_\tau=\omega_{e0},\omega_t=\omega_{eg}\right)\sim\mu^2_{0e}\mu^2_{eg}+\mu_{0e}\mu_{eg}\sum_{e'\neq e}\mu_{ge'}\mu_{0e'}e^{-i\omega_{ee'}T},$$

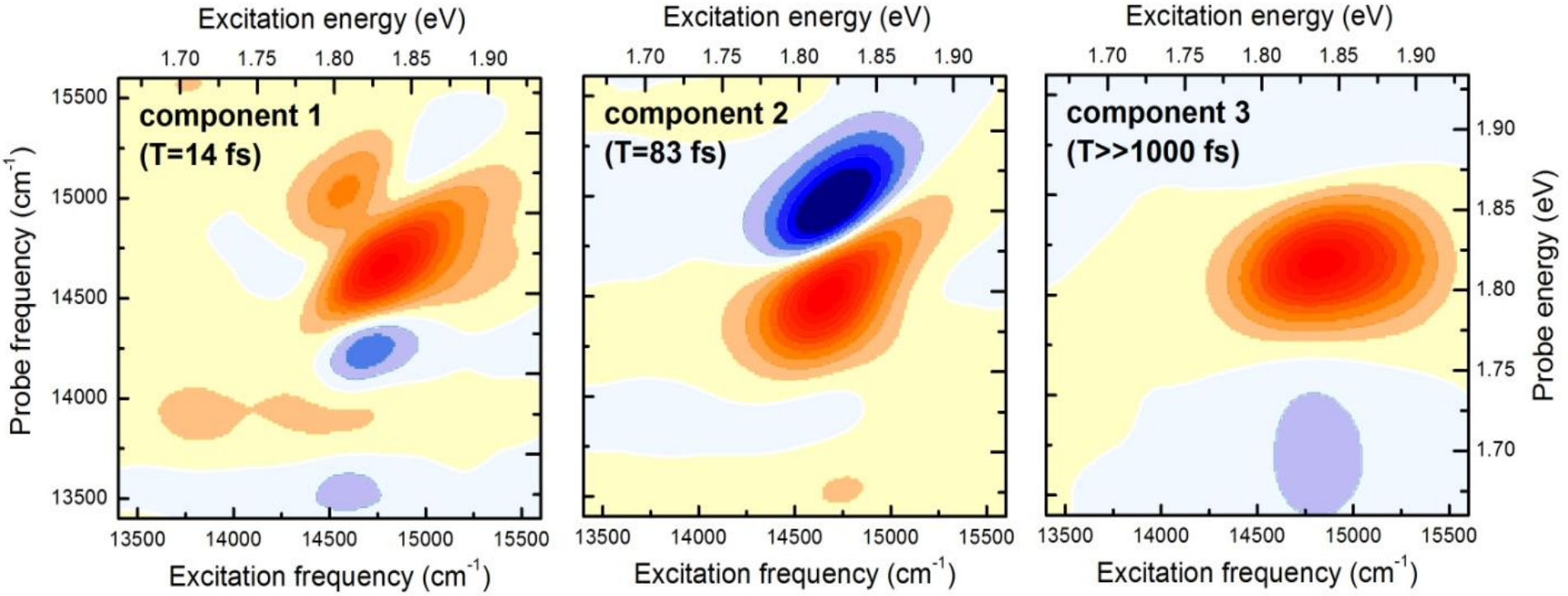
$$\mathrm{DP}^{\mathrm{GSB}}_{\mathrm{nonreph}}/\mathrm{CP}^{\mathrm{GSB}}_{\mathrm{nonreph}}\left(\omega_\tau=\omega_{e0},\omega_t=\omega_{e'0}\right)\sim\mu^2_{0e}\mu^2_{0e'}+\mu_{0e}\mu_{0e'}\sum_{g\neq 0}\mu_{eg}\mu_{ge'}e^{-i\omega_{g0}T}.$$

- There are many more dipole moments in 2D than in the absorption…
- some of them can be strong…

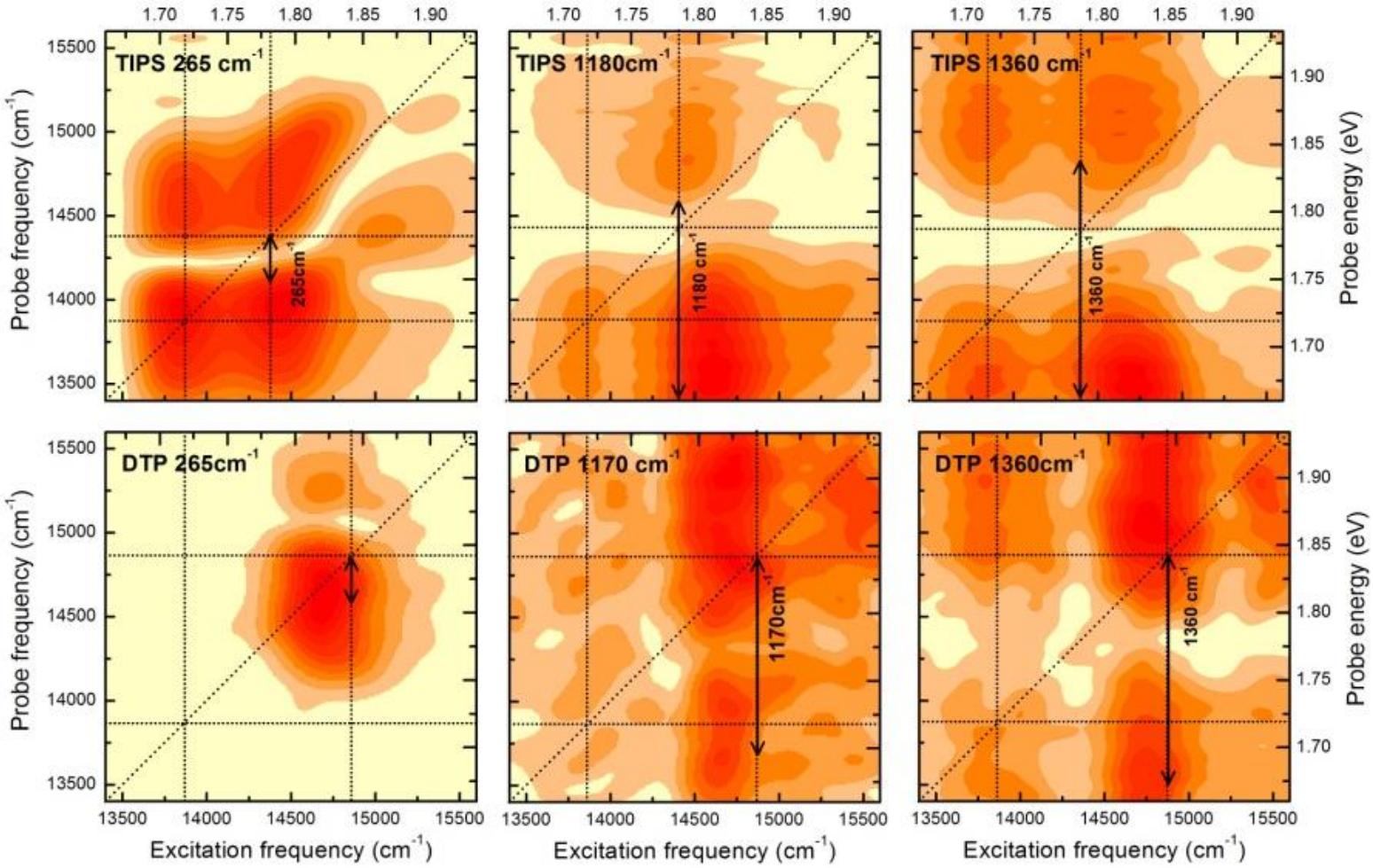


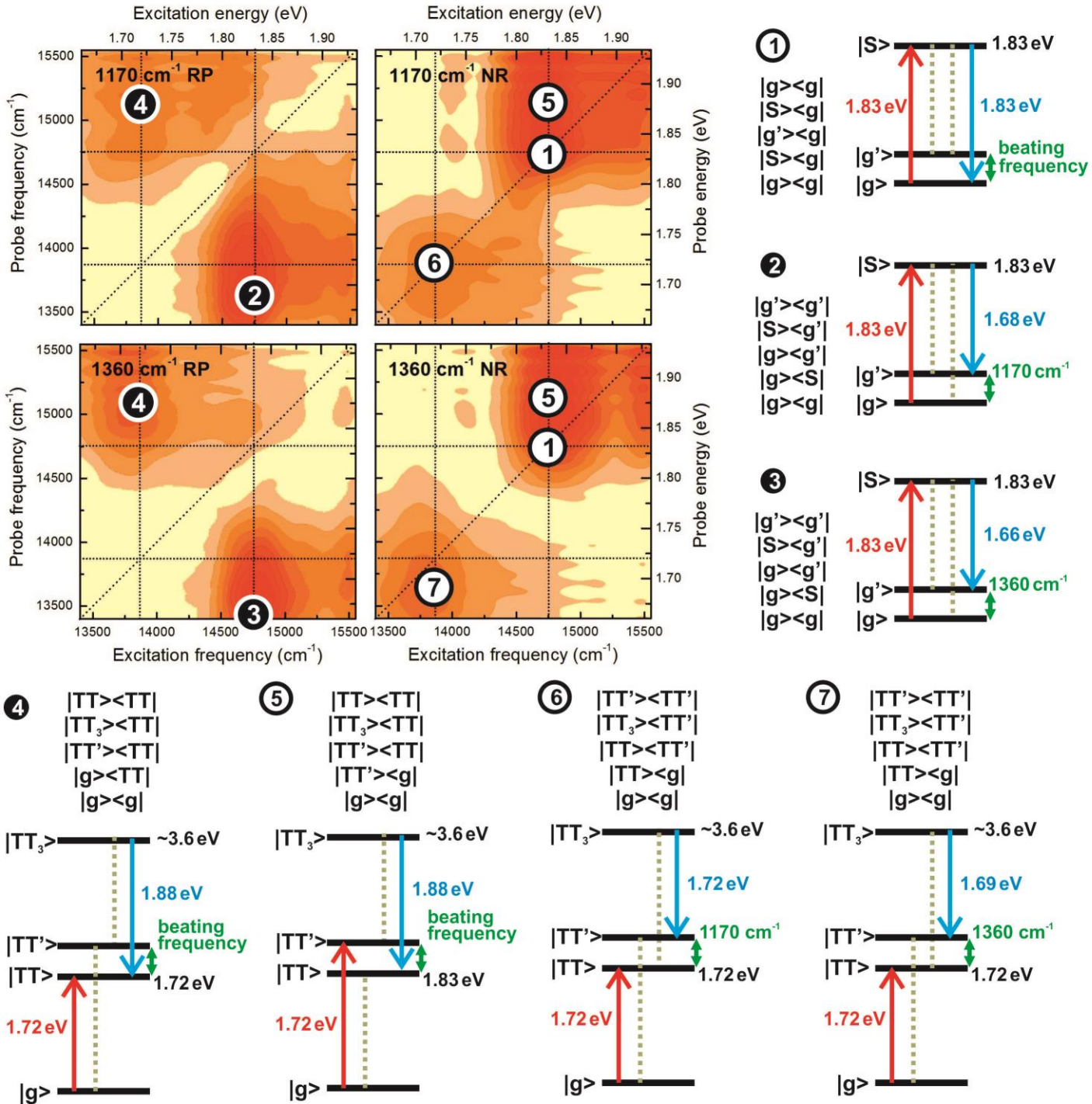
Deconvolution of different contributions

Coherent artifact ~Singlet Triplet

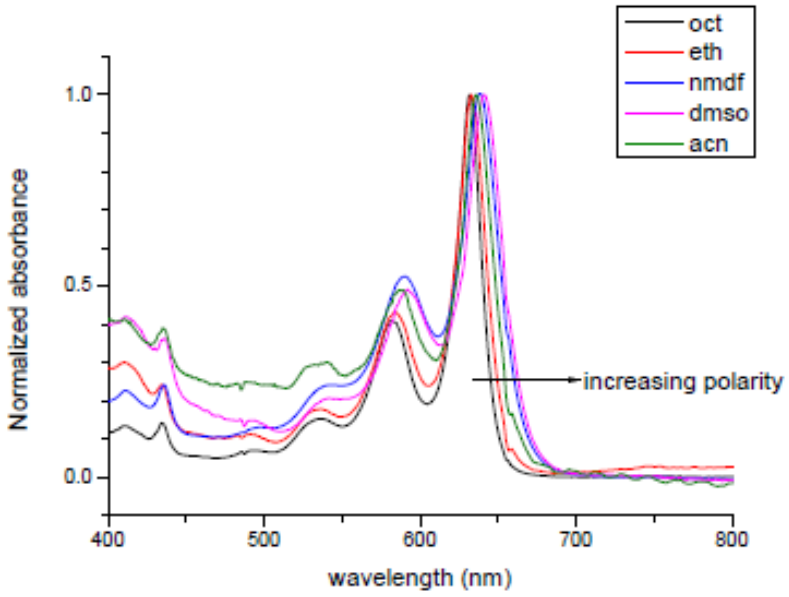


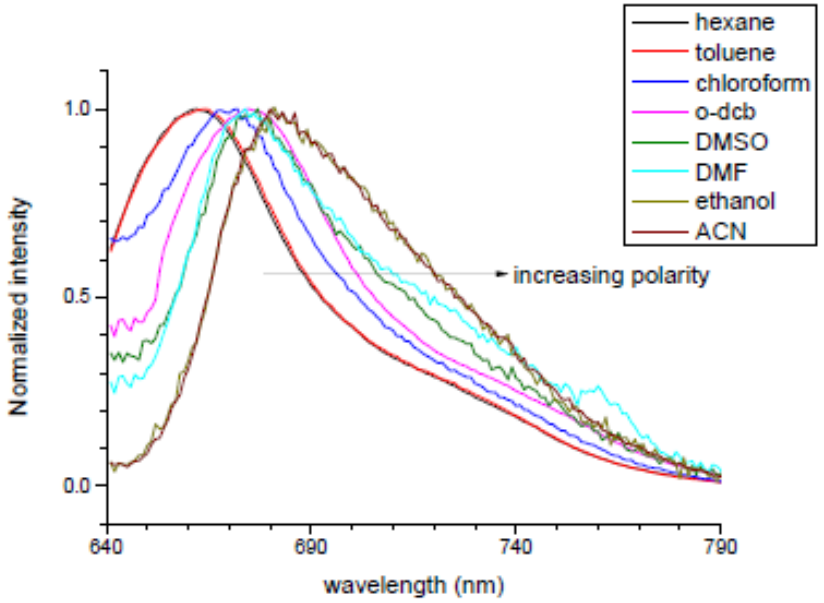
- 3 Components fully describe the data
- Fission happens in ~80fs (as we thought)


TIPS 265 cm-1
TIPS 1180cm-1
TIPS 1360 cm-1
DTP 265cm-1
DTP 1170 cm-1
DTP 1360cm-1
265cm-1
1180 cm-1
1360 cm-1
1170cm-1
1360 cm-1
Probe frequency (cm-1)
Probe energy (eV)
Excitation frequency (cm-1)
1.70
1.75
1.80
1.85
1.90
13500
14000
14500
15000
15500


Excitation energy (eV)
1.70 1.75 1.80 1.85 1.90
Probe frequency (cm-1)
15500 15000 14500 14000 13500
1170 cm-1 RP
1170 cm-1 NR
1360 cm-1 RP
1360 cm-1 NR
Probe energy (eV)
1.90 1.85 1.80 1.75 1.70
Excitation frequency (cm-1)
13500 14000 14500 15000 15500
1
|S><S|
|g><g|
|g'><g|
|S><g|
|g><g|
1.83 eV
1.83 eV
|g'>
beating frequency
|g>
2
|g'><g'|
|S><g'|
|g><g'|
|g><S|
|g><g|
1.68 eV
1170 cm-1
3
|g'><g'|
|S><g'|
|g><g'|
|g><S|
|g><g|
1.66 eV
1360 cm-1
4
|TT><TT|
|TT3><TT|
|TT'><TT|
|g><TT|
|g><g|
|TT3>
~3.6 eV
1.88 eV
|TT'>
|TT>
1.72 eV
|g>
5
|TT><TT|
|TT3><TT|
|TT'><TT|
|TT'><g|
|g><g|
1.83 eV
6
|TT'><TT'|
|TT3><TT'|
|TT><TT'|
|TT><g|
|g><g|
1.72 eV
1170 cm-1
7
|TT'><TT'|
|TT3><TT'|
|TT><TT'|
|TT><g|
|g><g|
1.69 eV
1360 cm-1

DP-TIPS (abs and PL spectra)





The revealed electronic structure: