# *Zien is geloven*

Wybren Jan Buma

*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam*
*Institute for Molecules and Materials, Radboud University*

# From molecule to society

Mol Phot

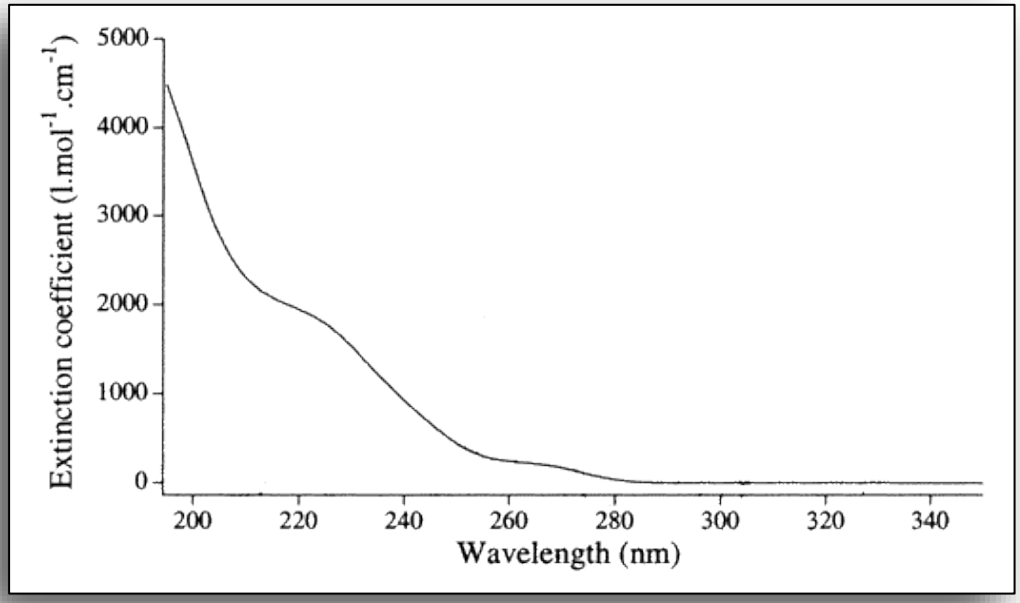


# Seeing is believing … but what are our eyes?

- Molecular fingerprints: absorption of electromagnetic radiation
  - *Microwaves (Nuclear Magnetic Resonance)*
    *nuclear spins as probes of spatial and chemical structure*
  - *Microwaves (rotational spectroscopy)*
    *distribution of mass in object*
  - *Infrared radiation (vibrational spectroscopy)*
    *internal structure, bond strengths, functional groups*
  - *UV/Vis (electronic spectroscopy)*
    *light absorbing chromophores, electronic distribution*

- How to achieve laser-limited resolution
  - *Molecular beams: isolated molecules at 0 K*
  - *Resonance Enhanced MultiPhoton Ionization Techniques*

# Spectroscopy: influence temperature and interactions



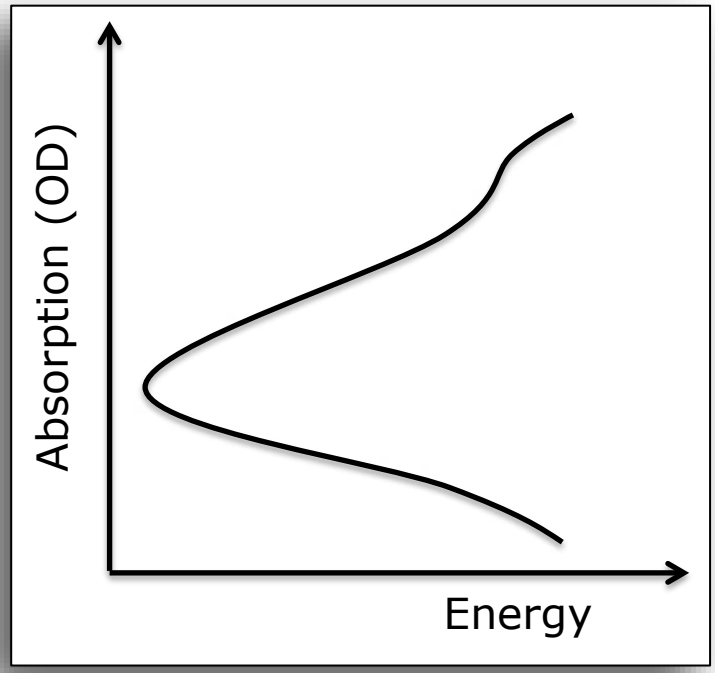

## Resolution limited by

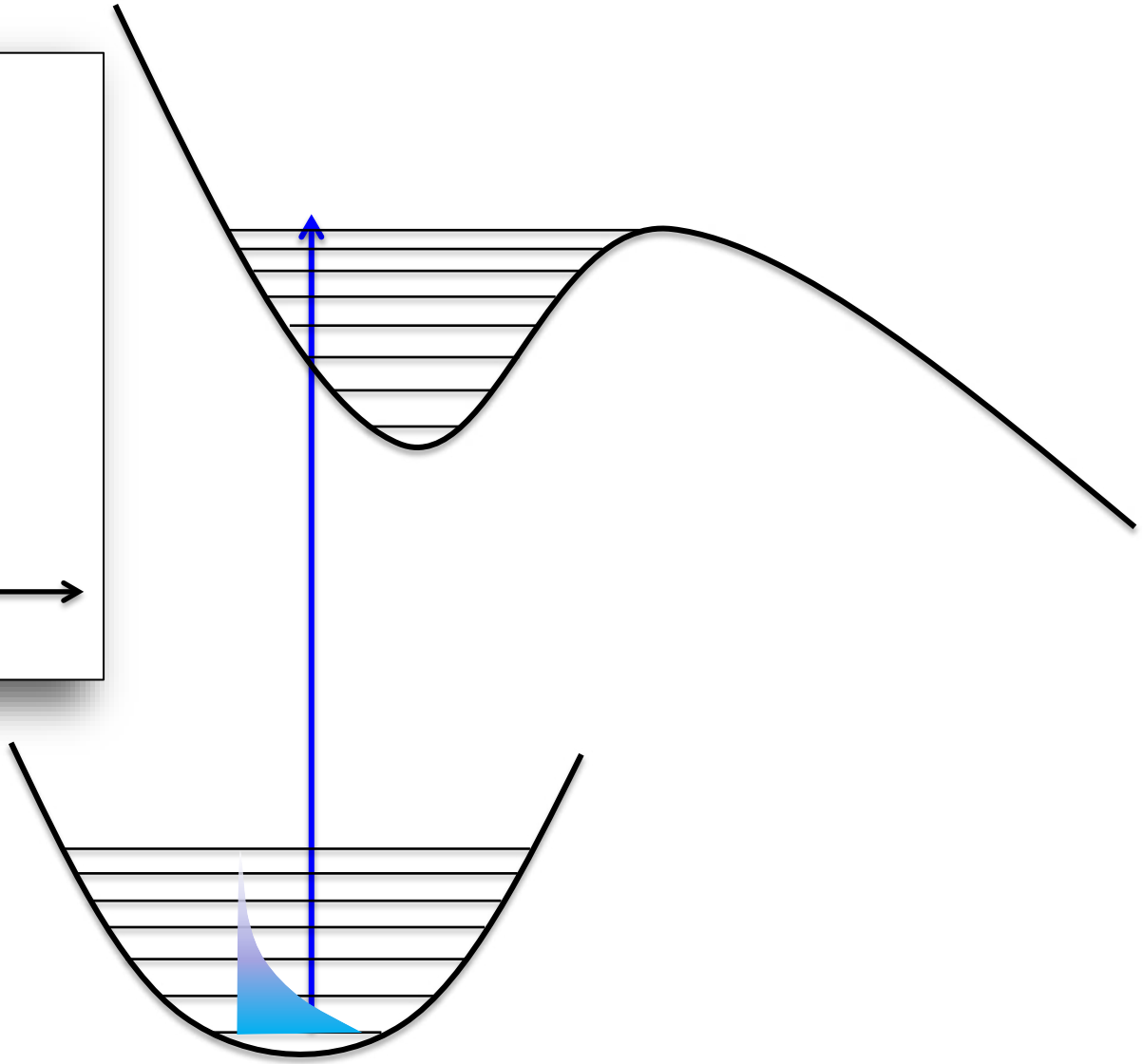
- *Many (rotational, vibrational) energy levels populated at room temperature*
- *Each molecule experiences slightly different environment*
- *Collisional broadening*

## Spectral consequences

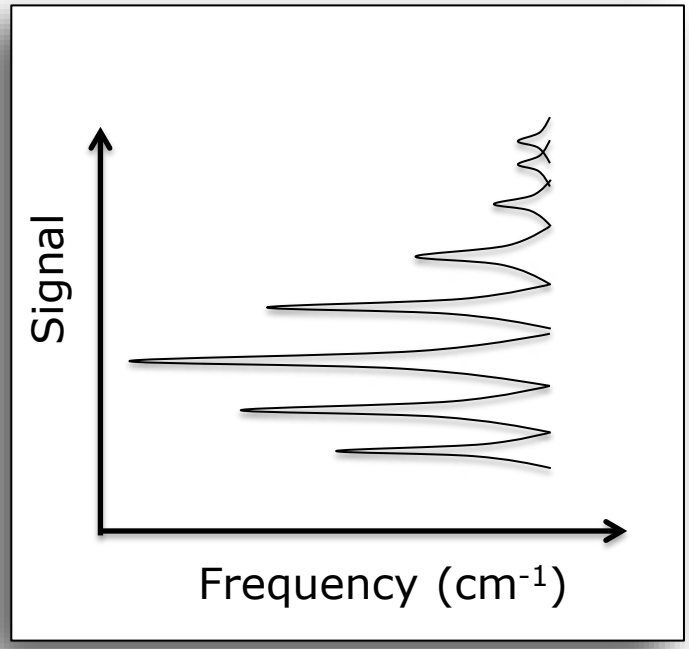
- *Each molecule absorbs at a different energy*
- *Linewidth determined by collisions*
- *Loss of spectral information on individual transitions*

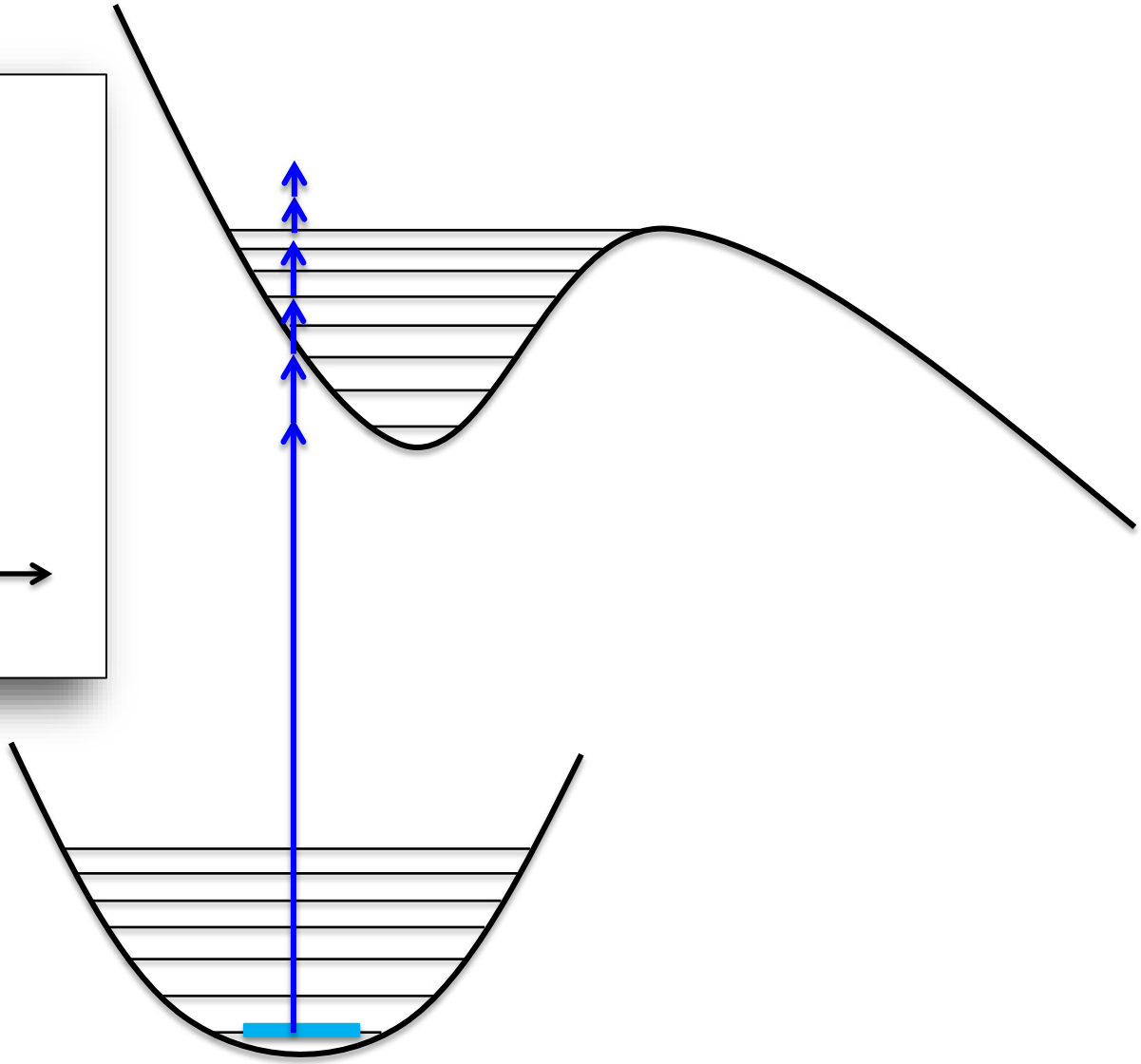
# Spectroscopy on non-isolated, room-temperature molecules



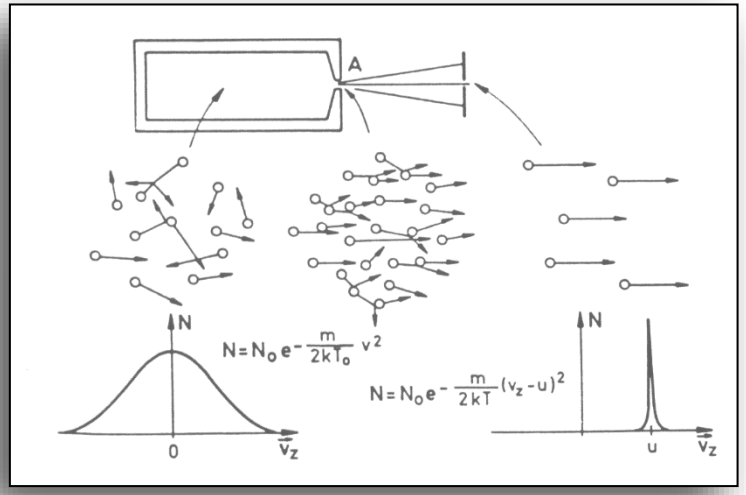



# Molecular beam spectroscopy



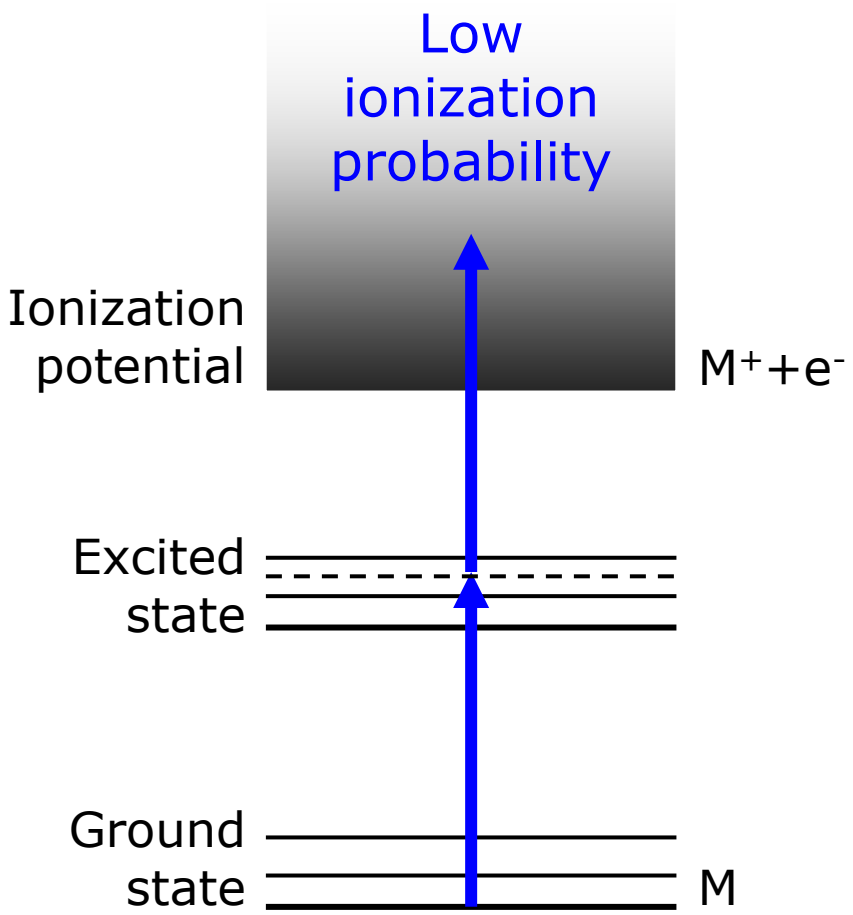
# Seeded supersonic expansions: cold and isolated molecules



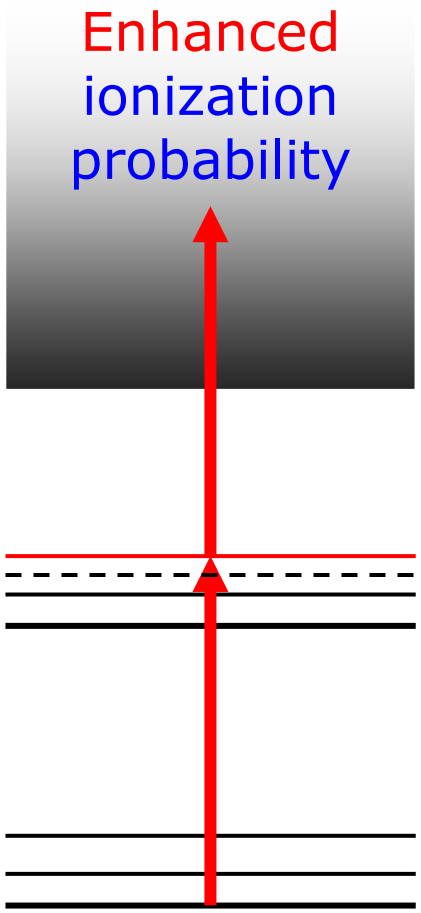
# Multiphoton ionization laser spectroscopy

Mol Phot

## *Non-resonant 2-photon ionization*

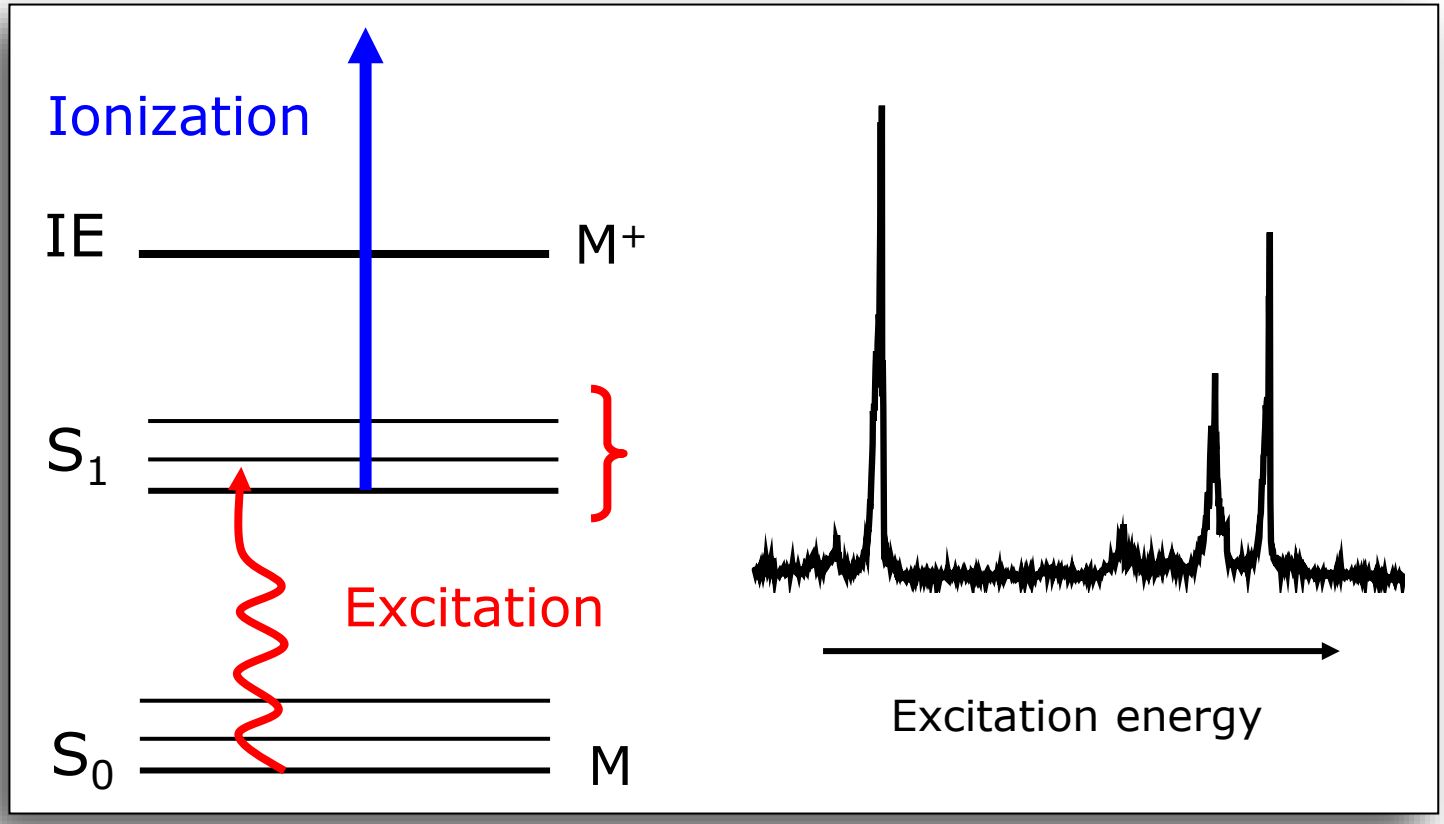



## *Resonance Enhanced (1+1) ionization*



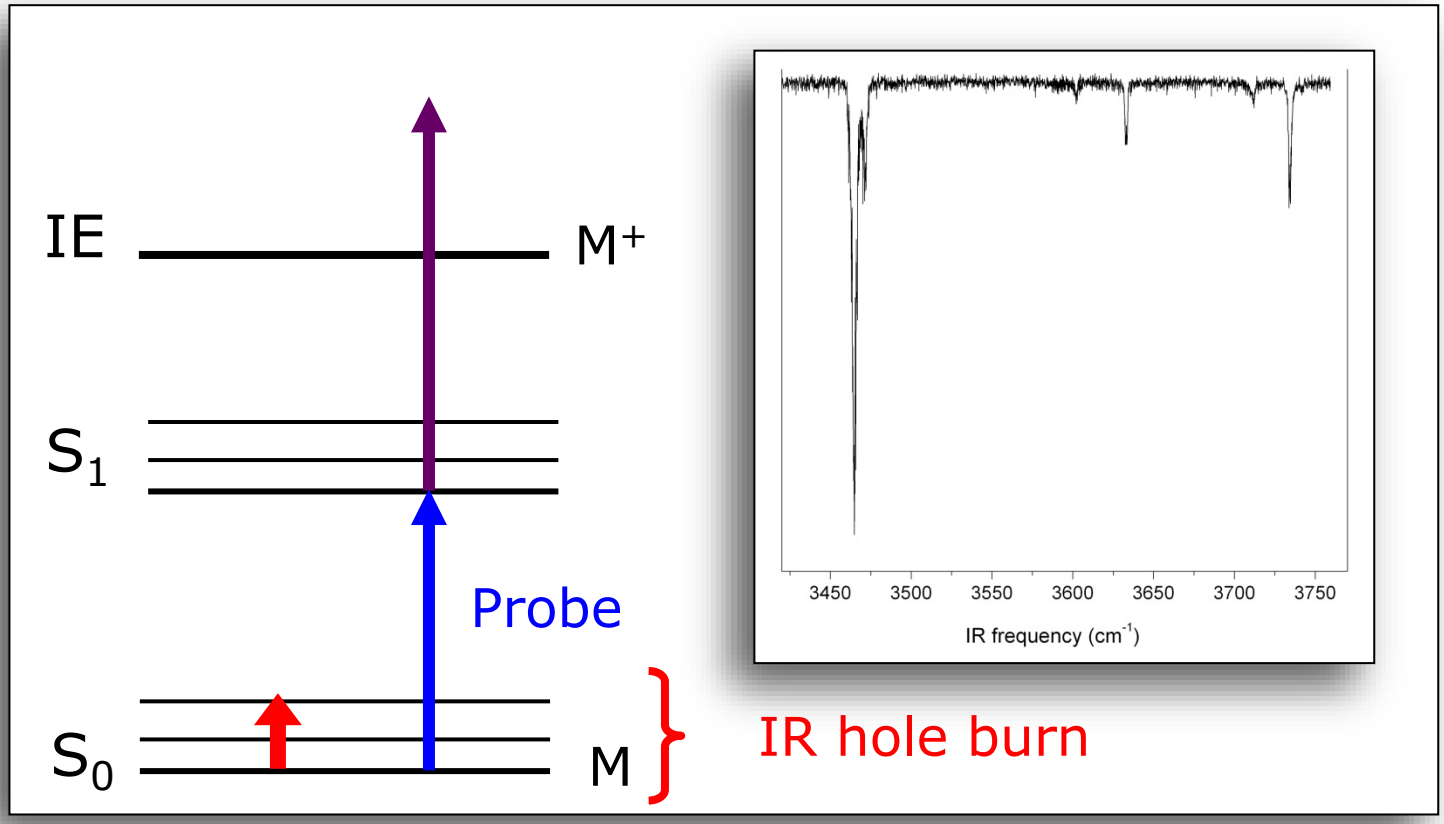
# Multiphoton ionization laser spectroscopy

*Mass-resolved spectroscopy under jet-cooled conditions*



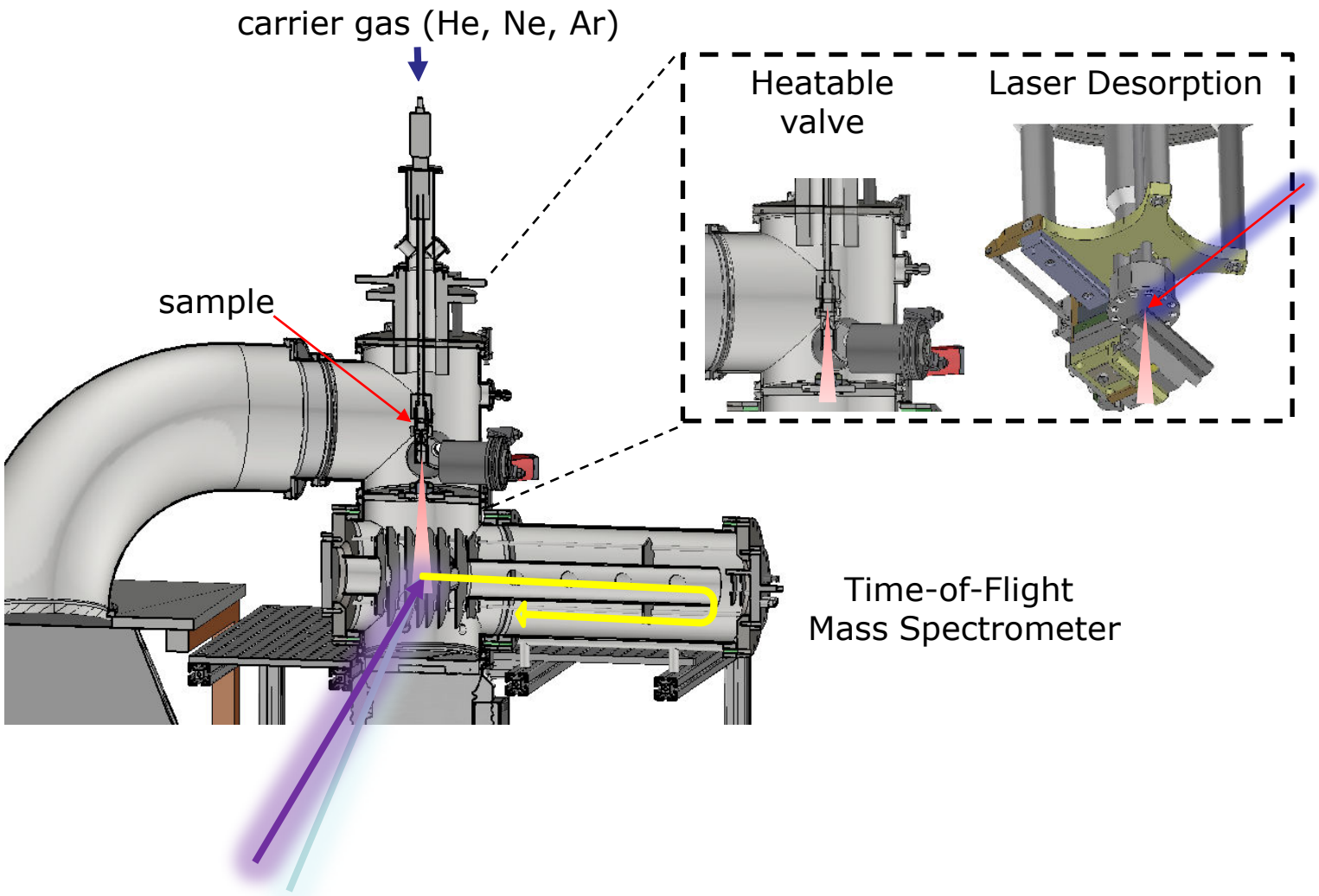
# IR ion dip spectroscopy

*Mass- and conformation-selective IR absorption spectroscopy*

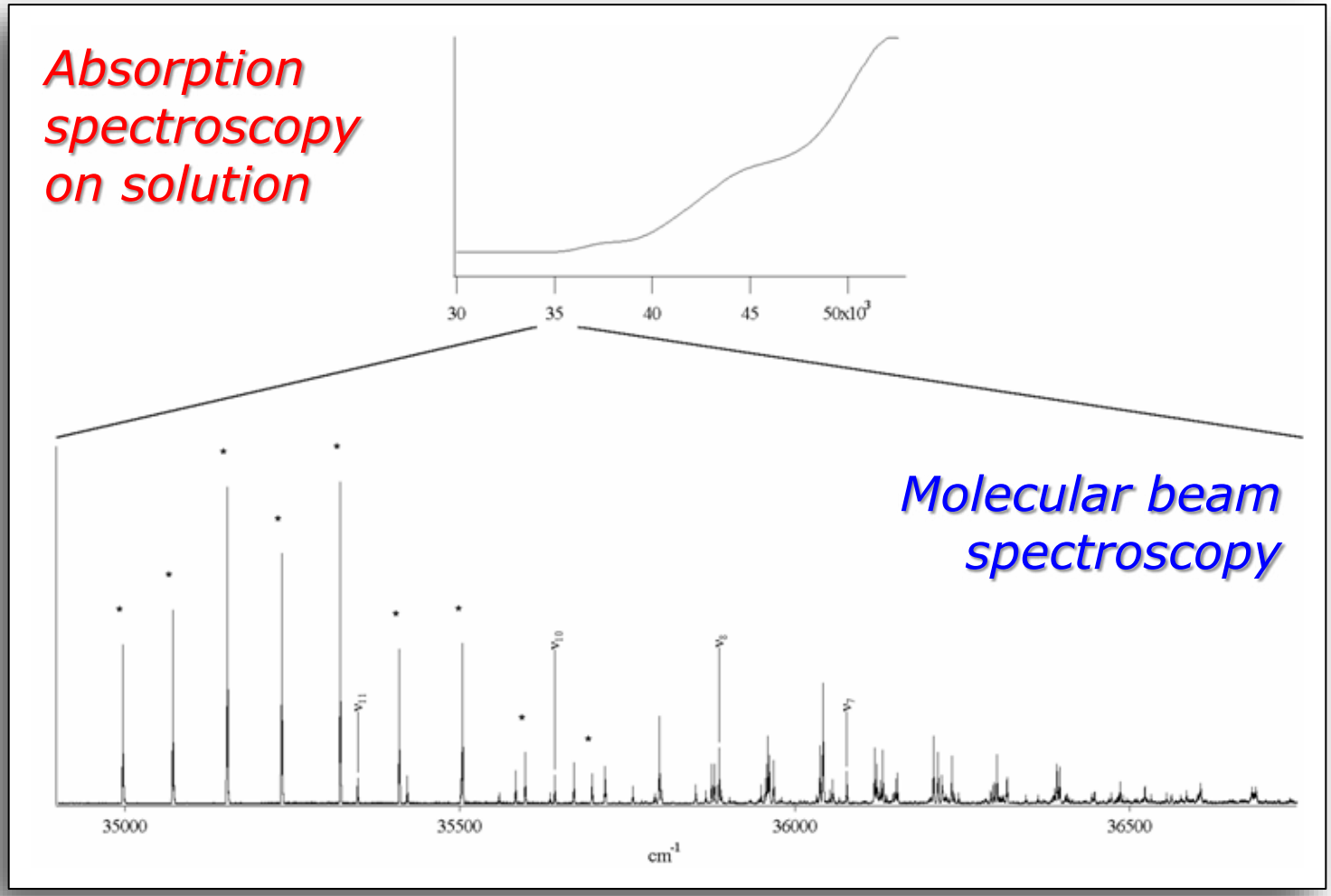


# Explore new molecular worlds

Mol Phot



# Uncovering what was hidden




*J. Am. Chem. Soc.* **2002**, *124*, 149

# High-resolution laser spectroscopy

Mol Phot

- **Bad vibrations at work in the universe**
  - *High-resolution IR absorption spectroscopy of Polycyclic Aromatic Hydrocarbons (PAHs)*
  - *Anharmonicity and astronomical observations*
- **The dark side of the force**
  - *Time-resolved spectroscopy in the frequency domain*
  - *Tracing photochemical reaction pathways*
- **Molecular heaters**
  - *Excited-state dynamics sunscreens*
  - *Boosting crop yields in horti- and agriculture*

# Interstellar PAHs: *in spectrometer* and *in silico*


***Elena Maltseva***
*(UvA)*

***Sander Lemmens***
*(UvA, RU, FELIX facility)*

***Cameron Mackie***, *Alessandra Candian, Xander Tielens (Leiden Observatory)*

*Annemieke Petrignani*
*(UvA, Leiden Observatory, FELIX facility)*

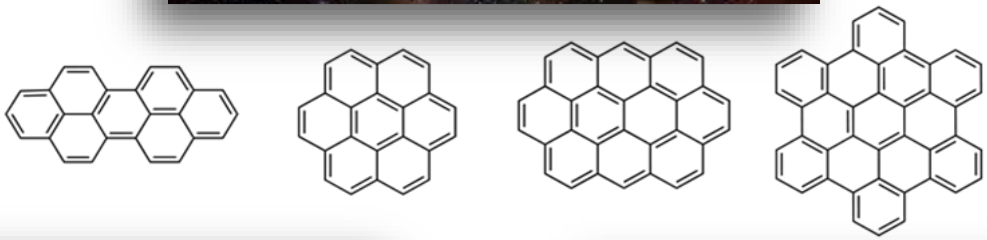
*Anouk Rijs, Jos Oomens, Giel Berden*
*(RU, FELIX facility)*

*Xinchuan Huang*
*(SETI Institute)*

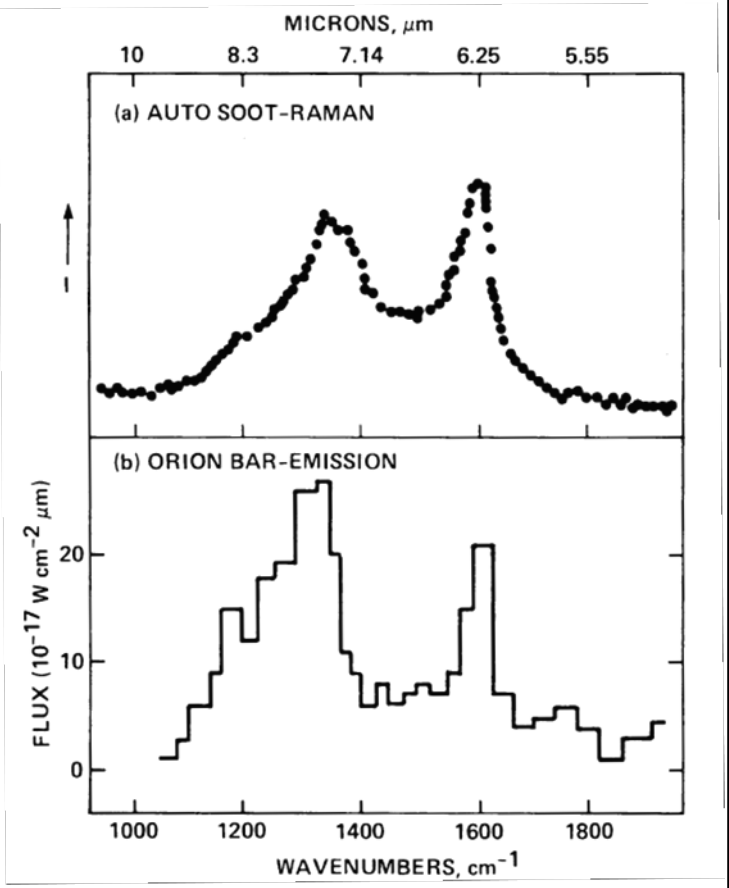
*Tim Lee*
*(NASA Ames Research Center)*

# Polycylic Aromatic Hydrocarbons

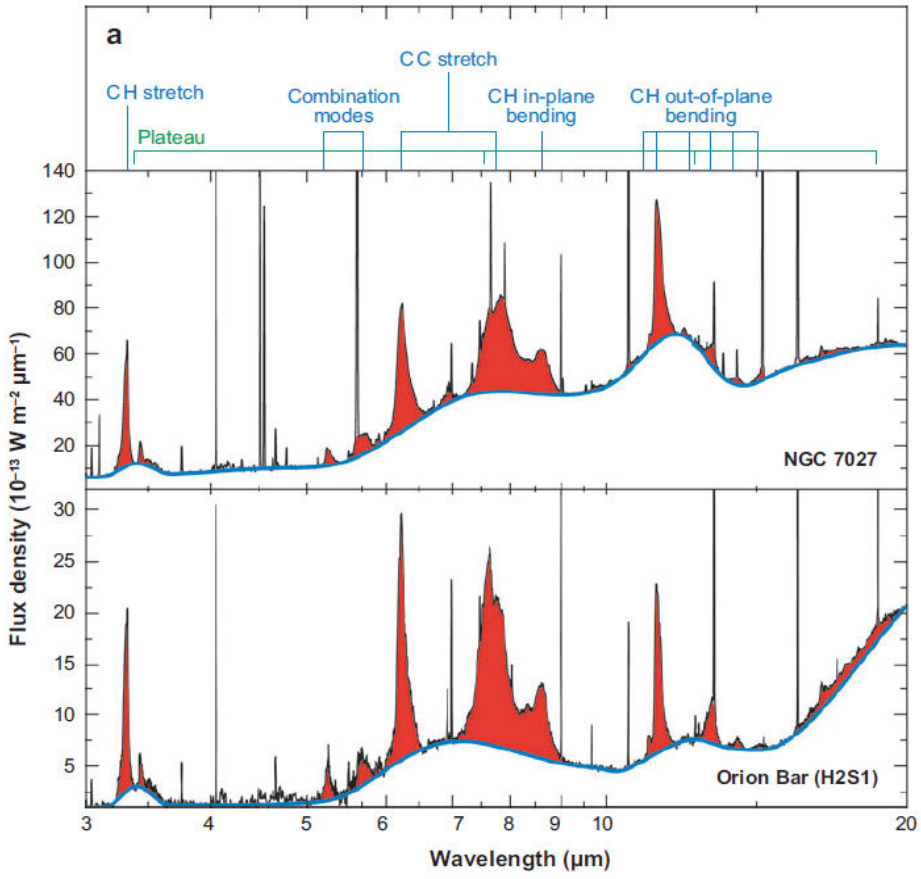
Mol Phot



# Auto exhaust along the Milky Way

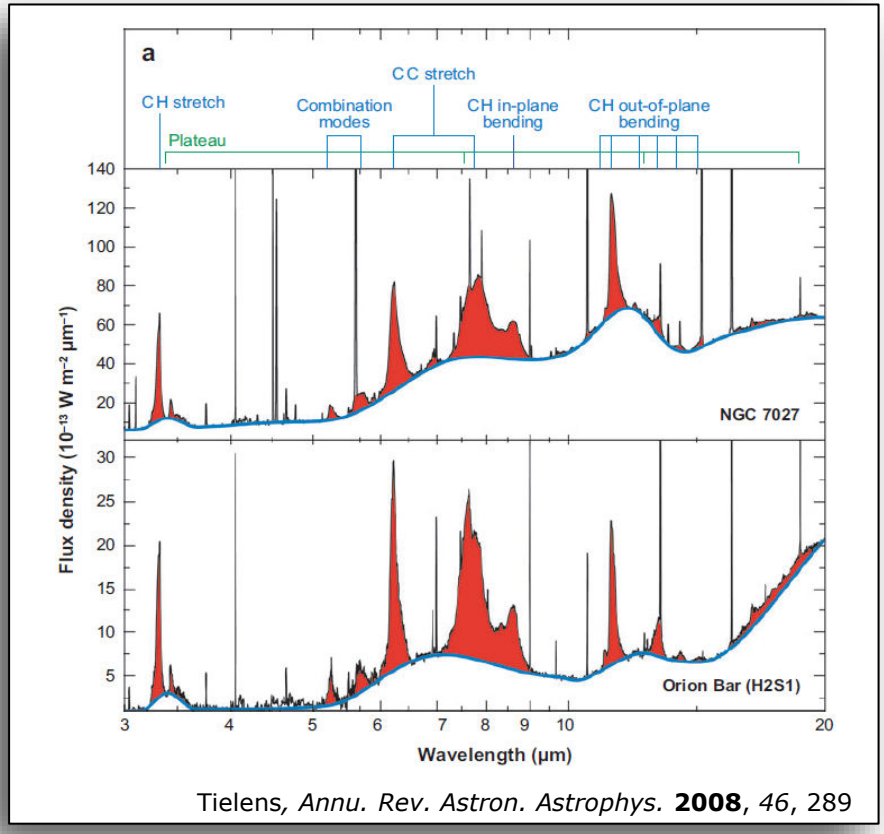



Allamandola *et al., Astrophys. J. Lett.* **1985**, *290*, L25




Tielens, *Annu. Rev. Astron. Astrophys.* **2008**, *46*, 289

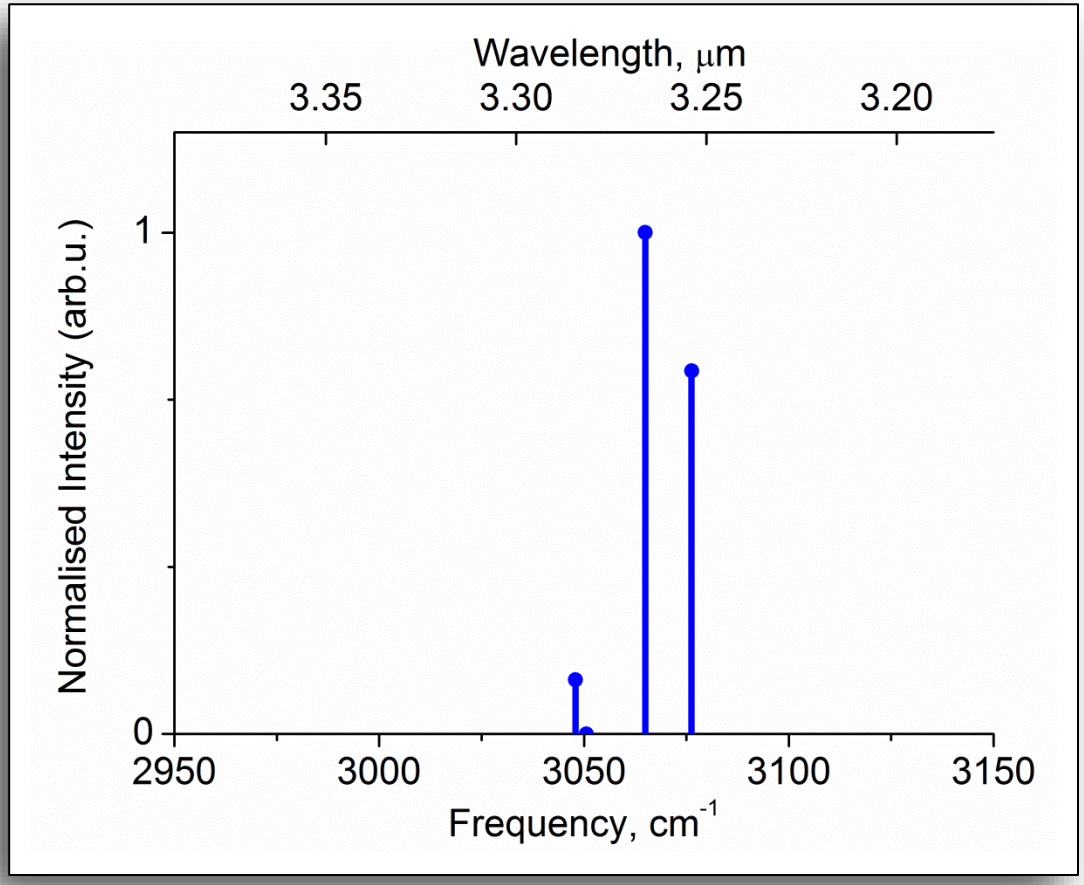
# Astronomical models

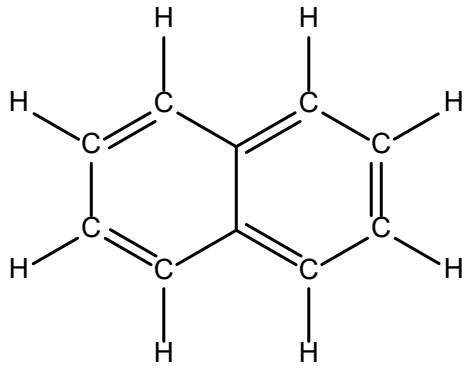



Tielens, *Annu. Rev. Astron. Astrophys.* **2008**, *46*, 289

- Band shapes and intensities modelled using *database* experimental and calculated PAH spectra
- Experimental spectra not compatible with astronomical conditions
  - *Spectral shifts and broadening in matrix*
  - *Loss of resolution at elevated temperatures*
- Calculations not compatible with *anharmonicity*
  - *Redistribution of intensities*

# Naphthalene:PAHs according to harmonic theory



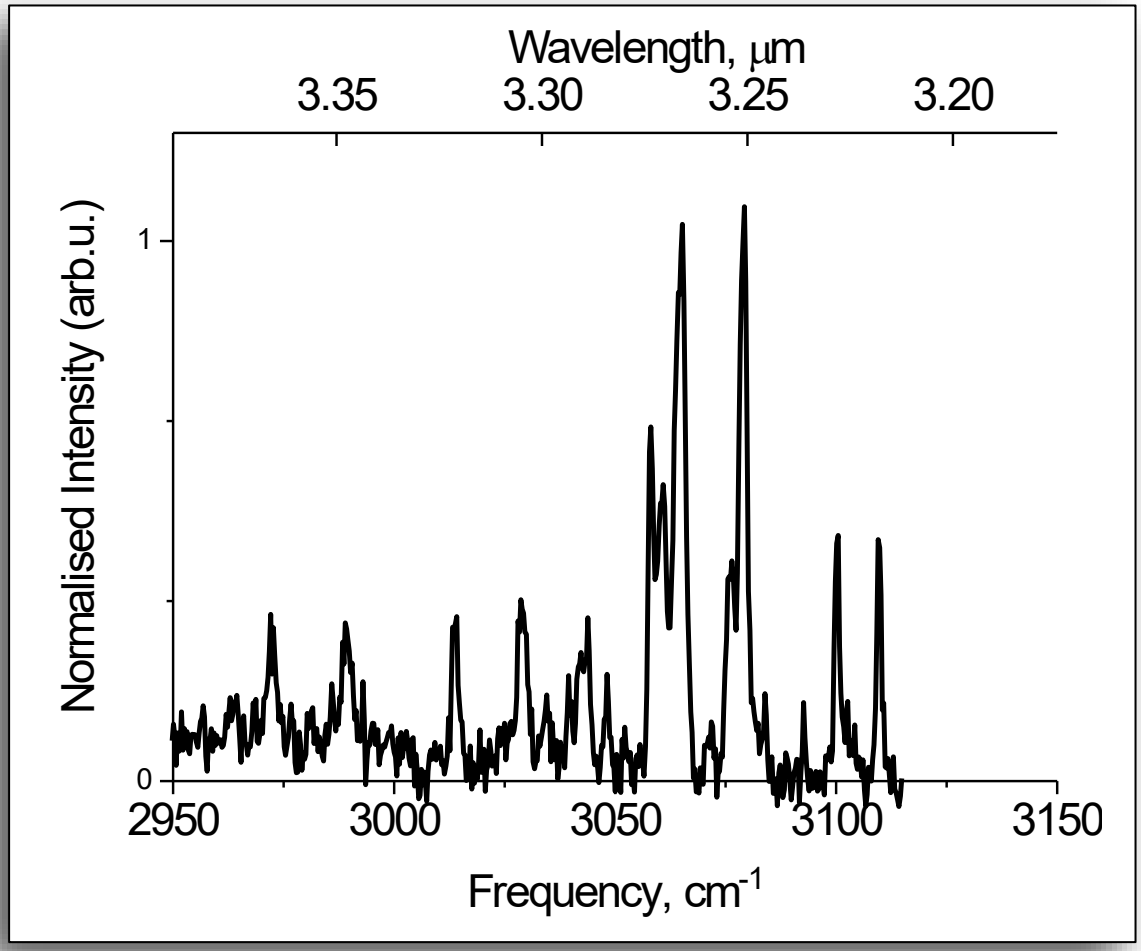




8 CH oscillators

$D_{2h}$ symmetry

4 IR-active modes

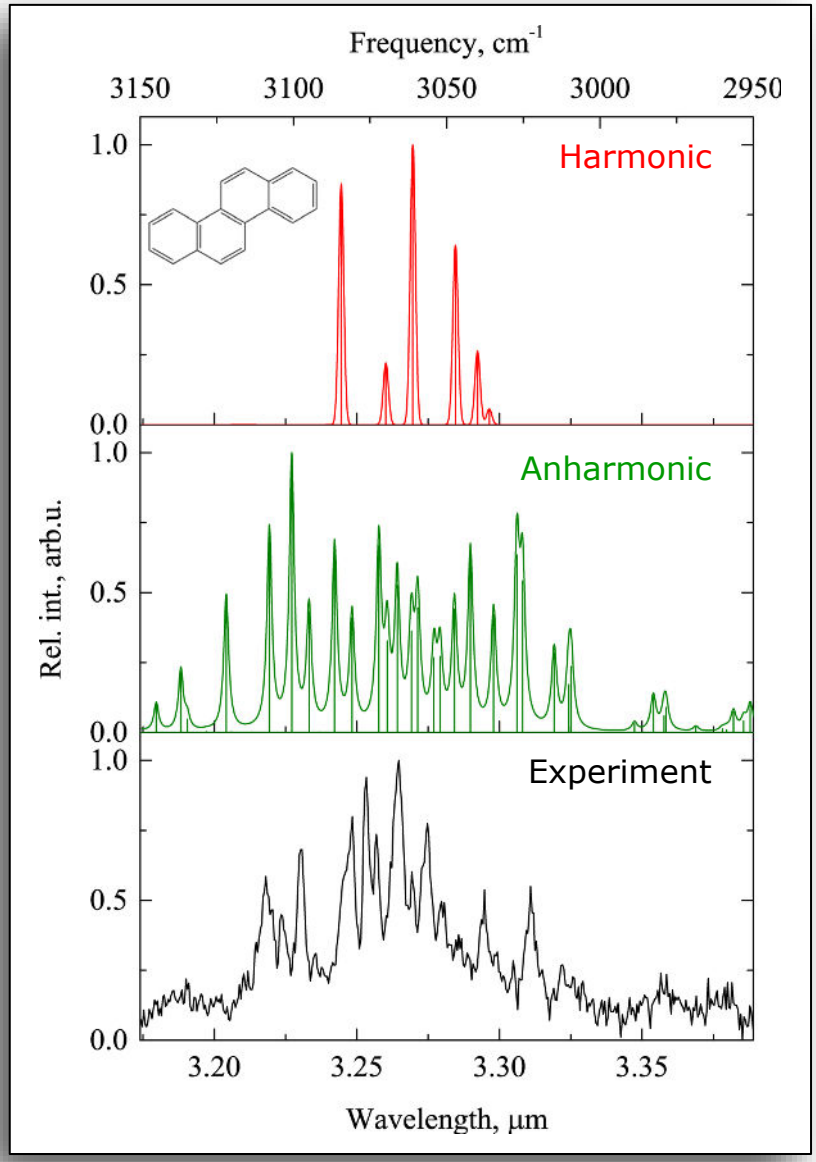
# Naphthalene:PAHs according to experiment




- **>23** bands
- *Anharmonicity* makes forbidden allowed
- *Intensities* order of magnitude larger than predicted

*Astrophys. J.* **2015**, *814*, 23

# Experiments and theory under astronomical conditions



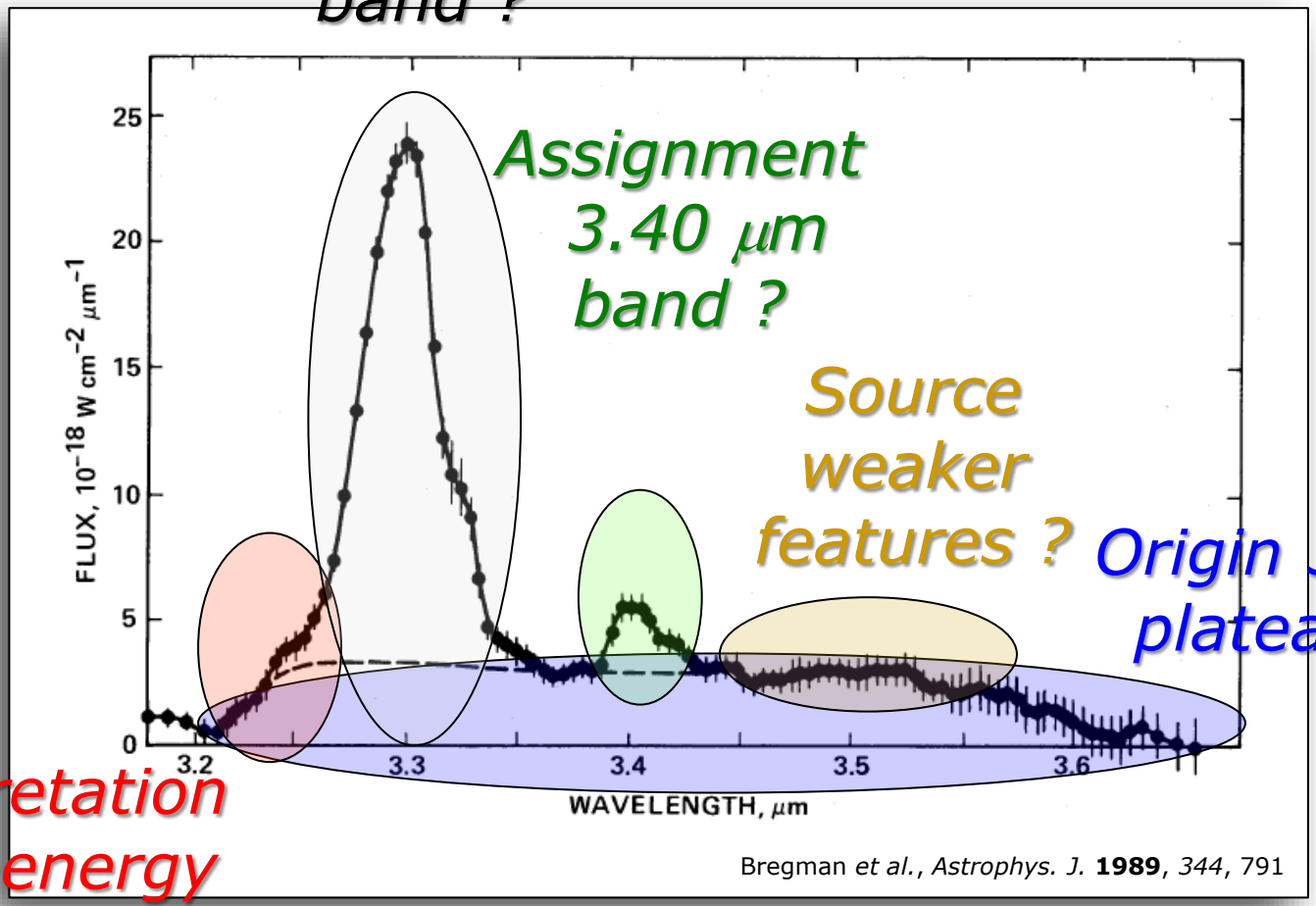

- *Superior resolution* experimental spectrum
- Anharmonicity determines intensity distribution 3 μm band
  - *Harmonic spectrum misses essential features experiment*
  - *Anharmonic spectrum in excellent agreement*
- Assignment individual bands powerful tool to *disentangle spectra*
- *Database in-silico spectra* realistic tool for building astronomical models

*Astrophys. J.* **2016**, *831*, 58
*J. Chem. Phys.* **2016**, *145*, 084313

# Enigmas 3 μm band Polycyclic Aromatic Hydrocarbons

Mol Phot

*Shape 3.29 μm band ?*




*Assignment 3.40 μm band ?*

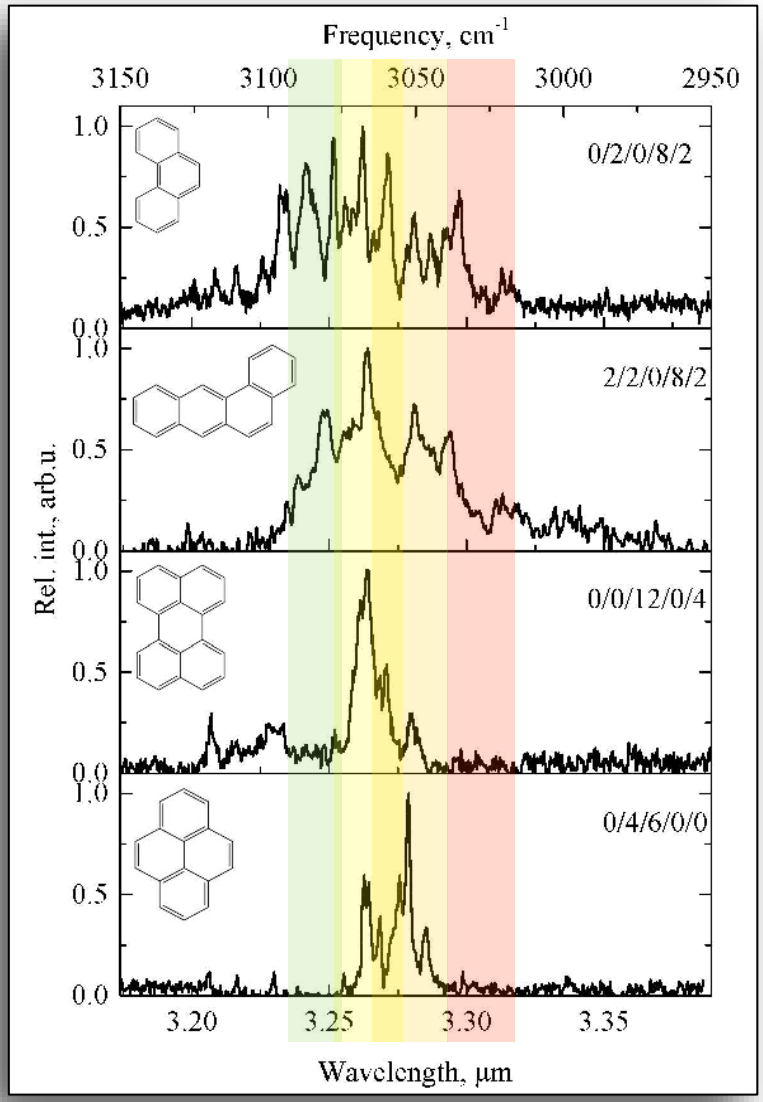
*Source weaker features ?*

*Origin 3 μm plateau ?*

*Interpretation high-energy wing ?*

Bregman *et al.*, *Astrophys. J.* **1989**, *344*, 791

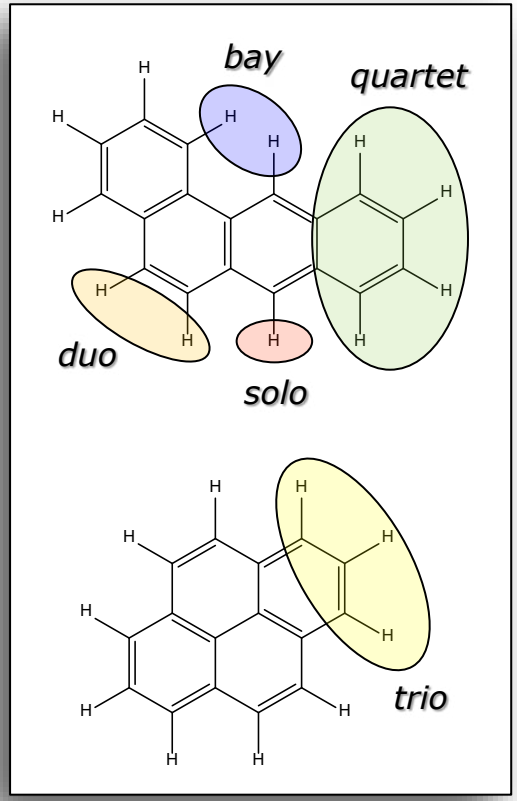
# Spectral analysis in terms of C-H sites




*Confined frequency regions*

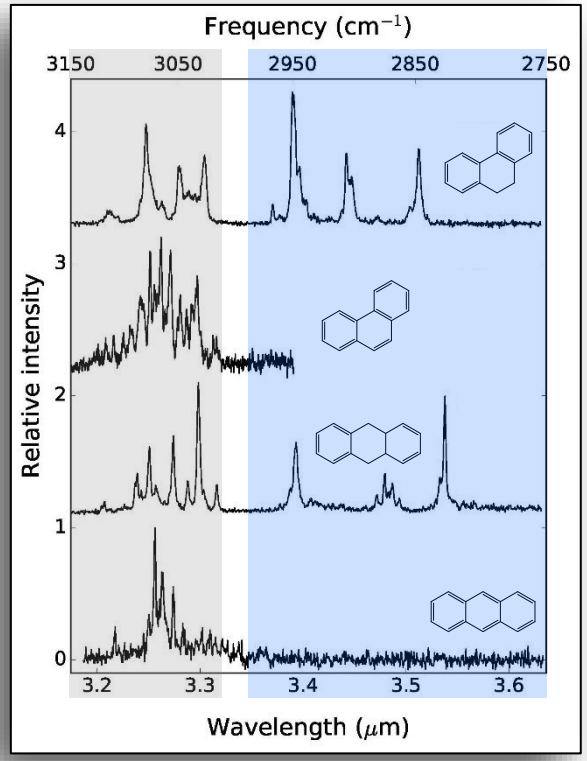
different C-H sites

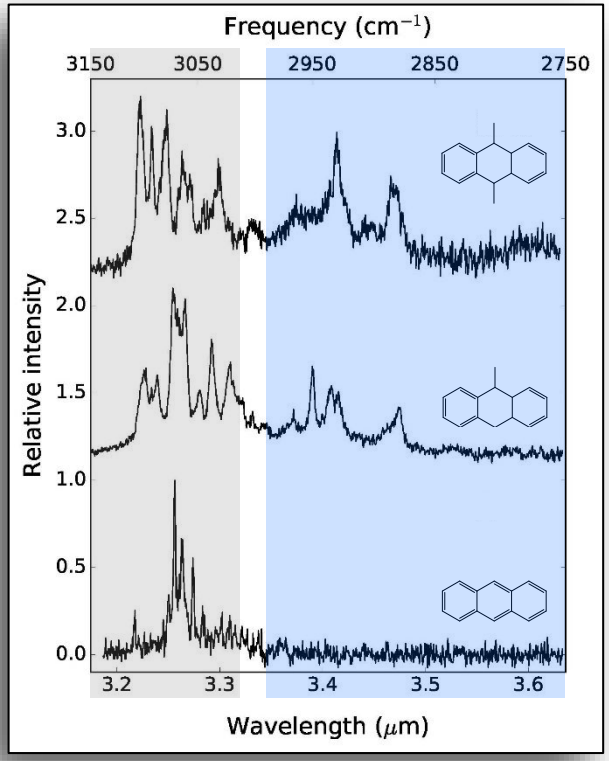
$$\nu_{\text{solo}} < \nu_{\text{duo}} < \nu_{\text{trio}} < \nu_{\text{quartet}}$$




*Astrophys. J.* **2015**, *814*, 23; **2016**, *831*, 58
*J. Chem. Phys.* **2015**; *143*, 224314; **2016**, *145*, 084313

# Effects of hydrogenation and methylation

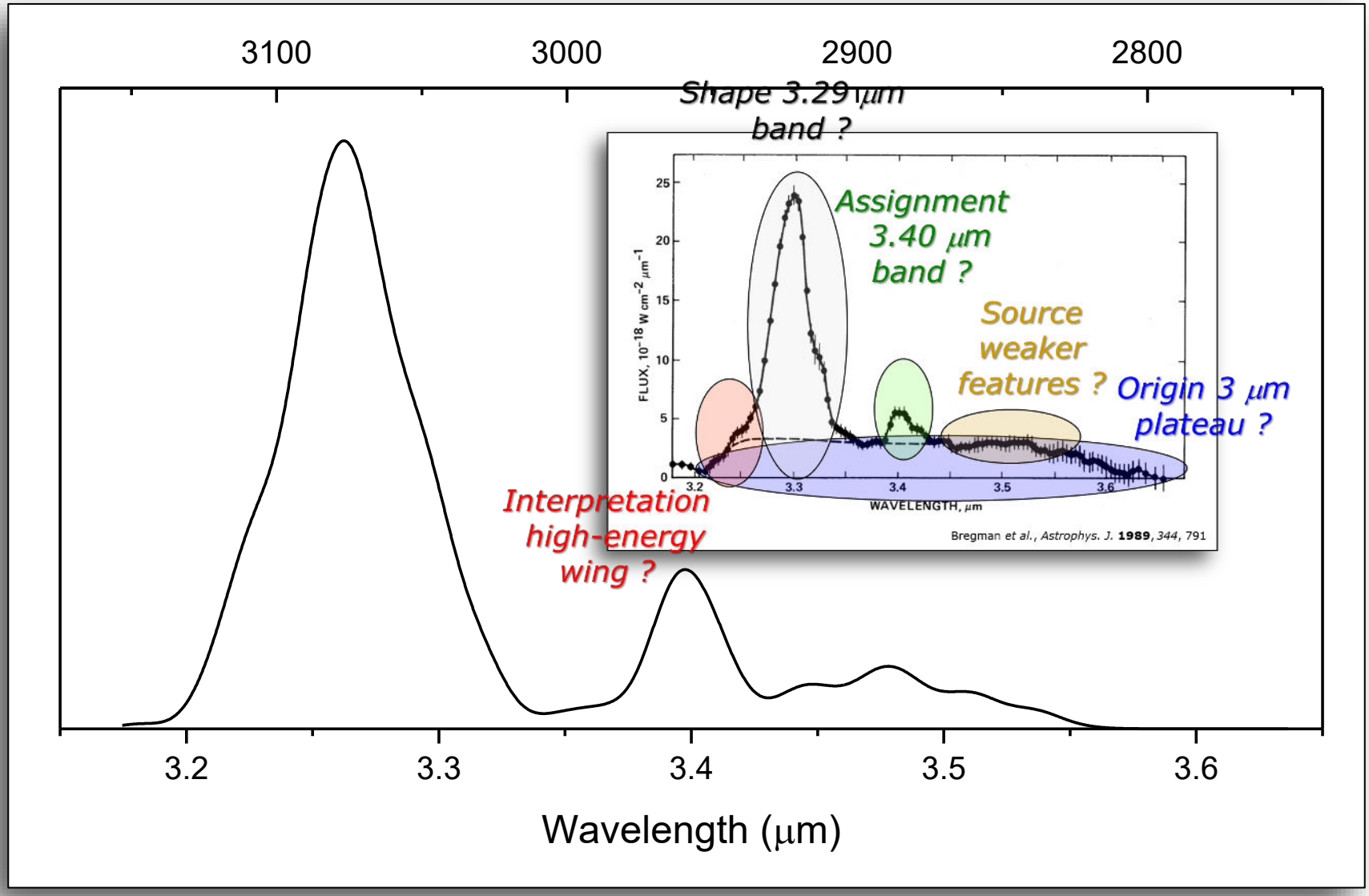


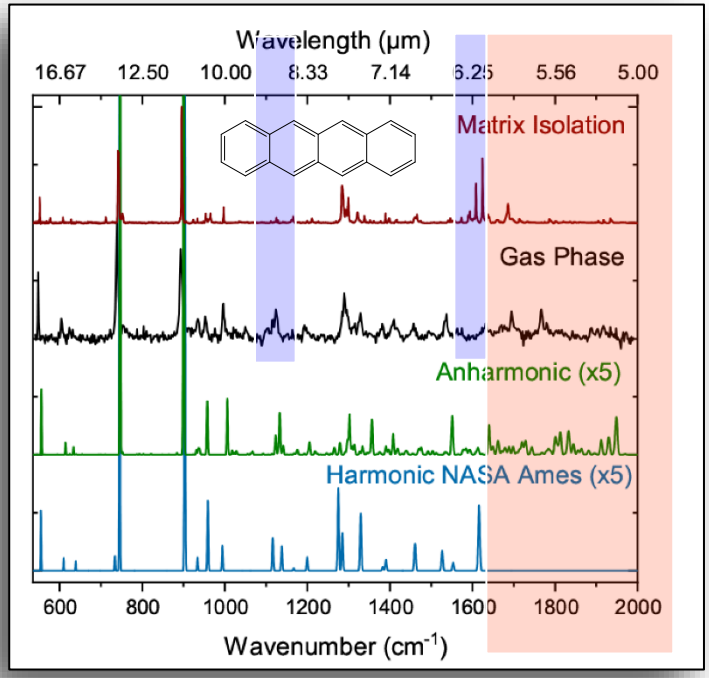

- Induces strong IR activity *below ~3000 cm$^{-1}$*
- *Aliphatic* region ruled by *Fermi resonances*
- *Aromatic* region subject to *significant changes*
  - *symmetry lowering and steric hindrance*
  - *redistribution intensity over combination bands*

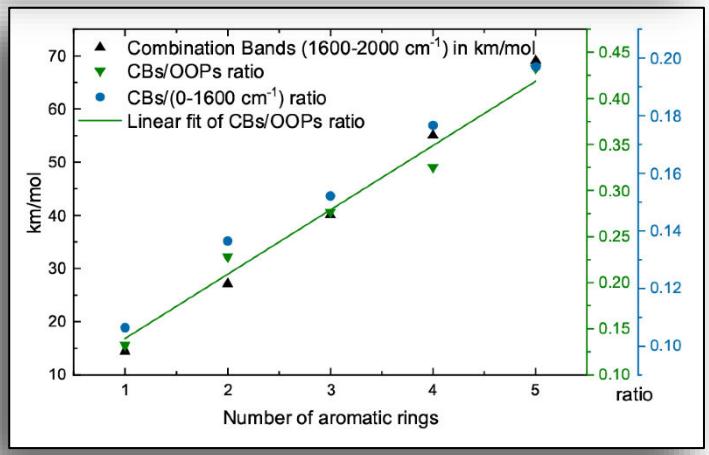
*Astron. Astrophys.* **2018**, *610*, A65
*Phys. Chem. Chem. Phys.* **2018** *20*, 1189

# 3 μm IR absorption spectrum "Elena Nebula"



# Anharmonicity in the mid-IR region

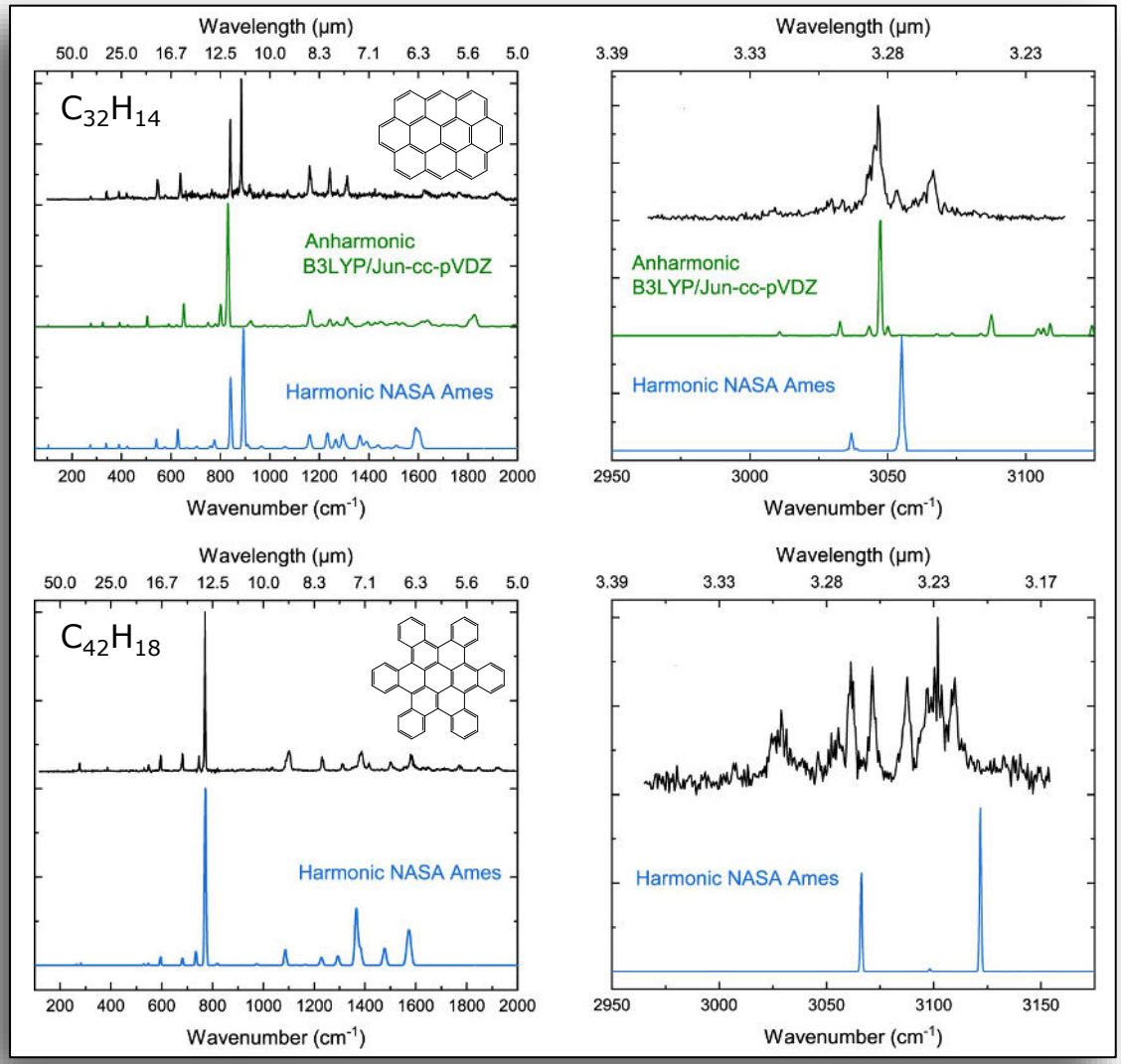


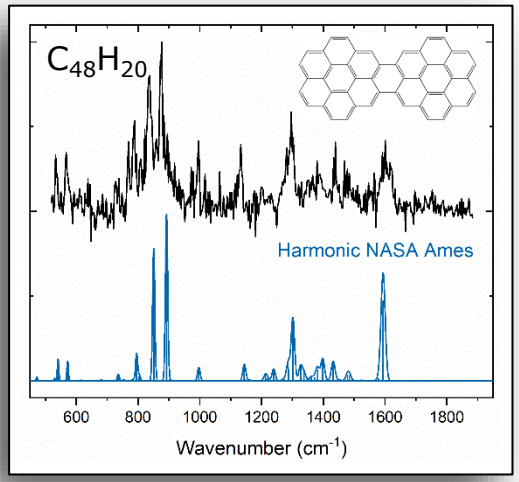




- Significant activity *'no-man's land'*
- Large *influence matrix* on relative intensities
- Calculations indicate *increase integrated 'no-man's land' activity* for larger PAHs
- Astronomically observed 5.25 and 5.7 μm bands suggest ***large similarity periphery***

*Astron. Astrophys.* **2019**, *628*, A130

# From baby- and puberty-PAHs to young grandPAHs

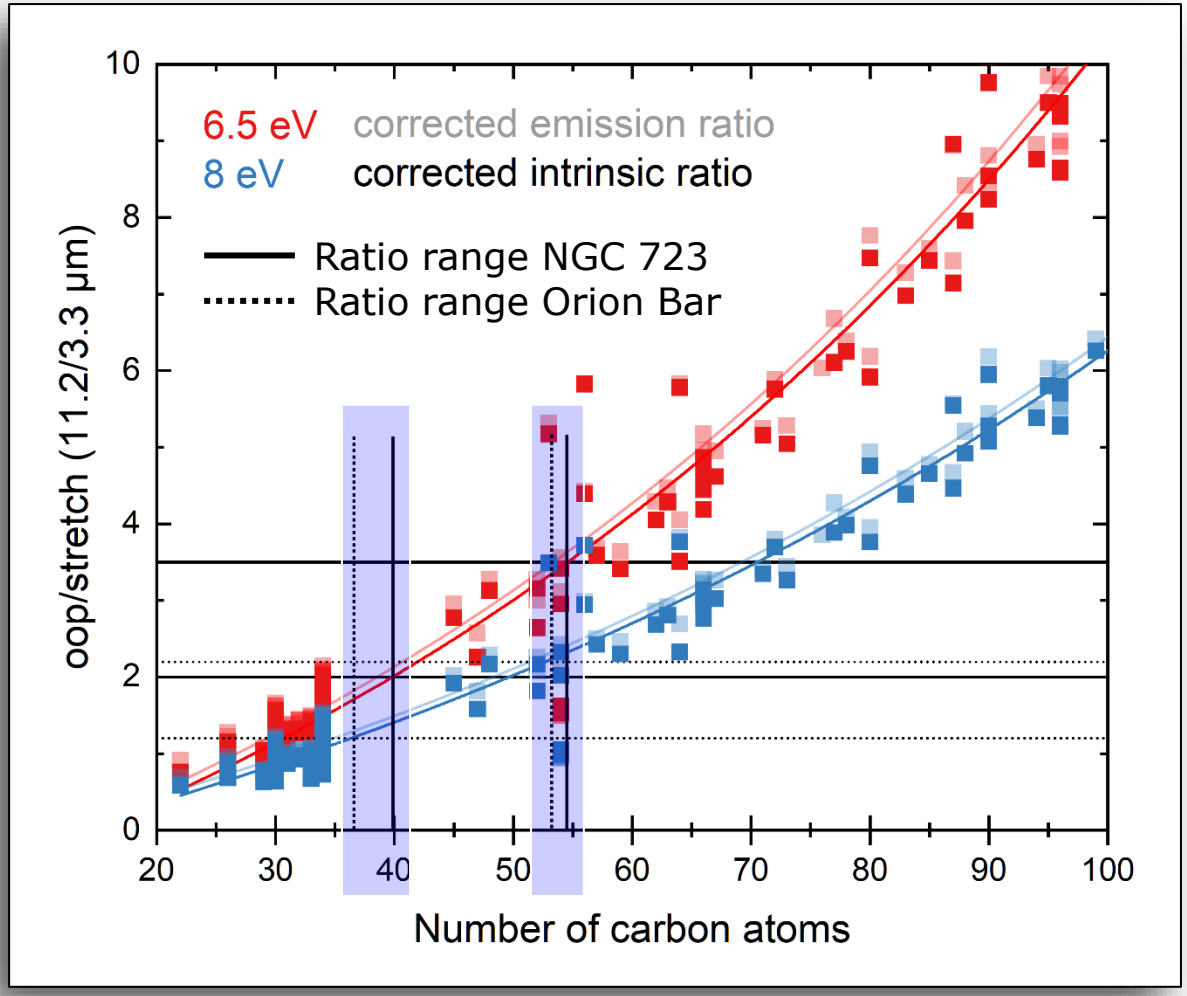



- Better agreement harmonic calculations
- Anharmonicity essential for 5-6 μm and CH-stretch
- *Anharmonic calculations challenge*

*Astrophys. J.* **2021**, *923*, 238; *Lemmens et al.*, unpublished

# Astronomical grandPAHs: centenials or just retired?




## Size distribution

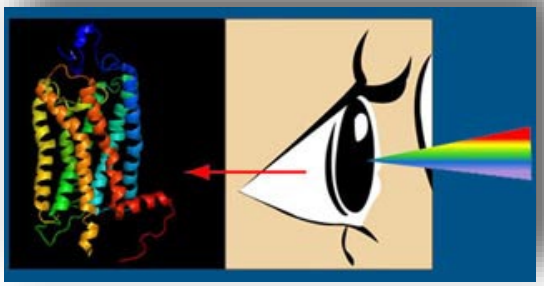
Original range:
*50-70 atoms*

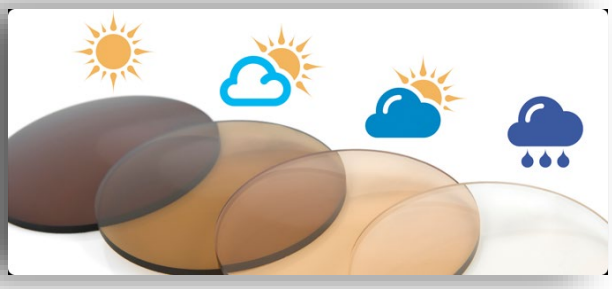
Corrected range:
*40-55 atoms*

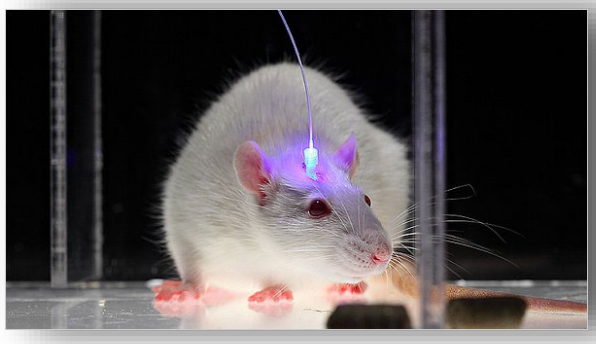
*Lemmens et al.*, to be published

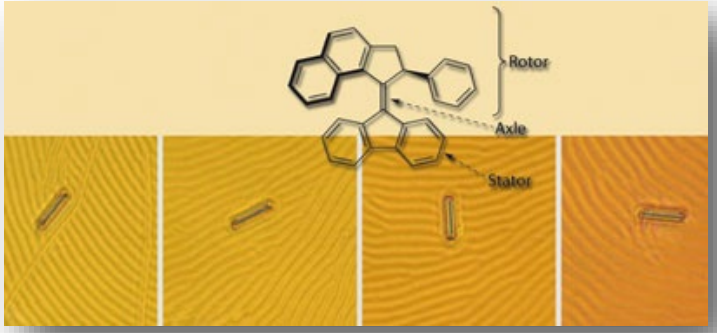
# Molecules and light

Mol Phot

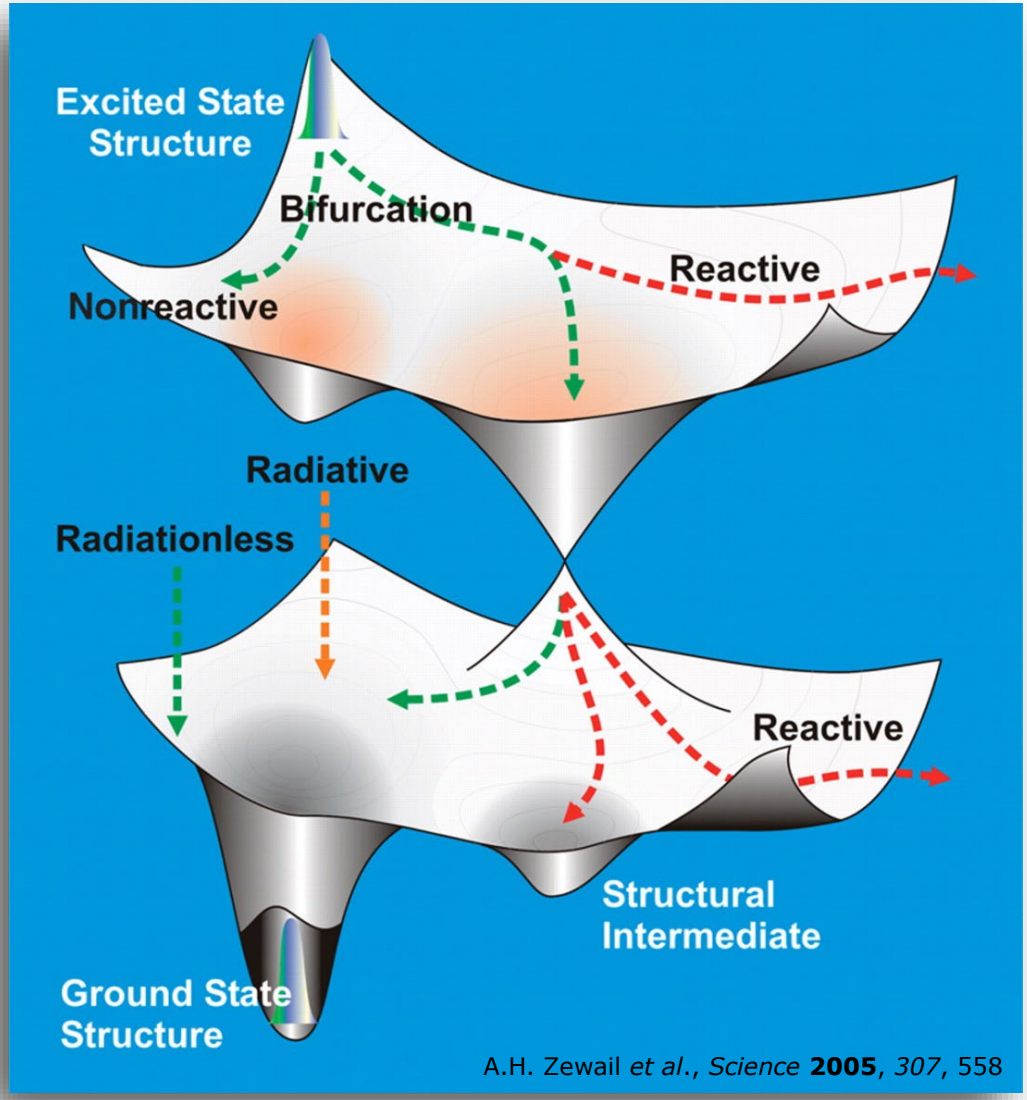






# Photons at work




Light-to-activity path determined by potential energy surfaces electronically excited states

# Conical intersections

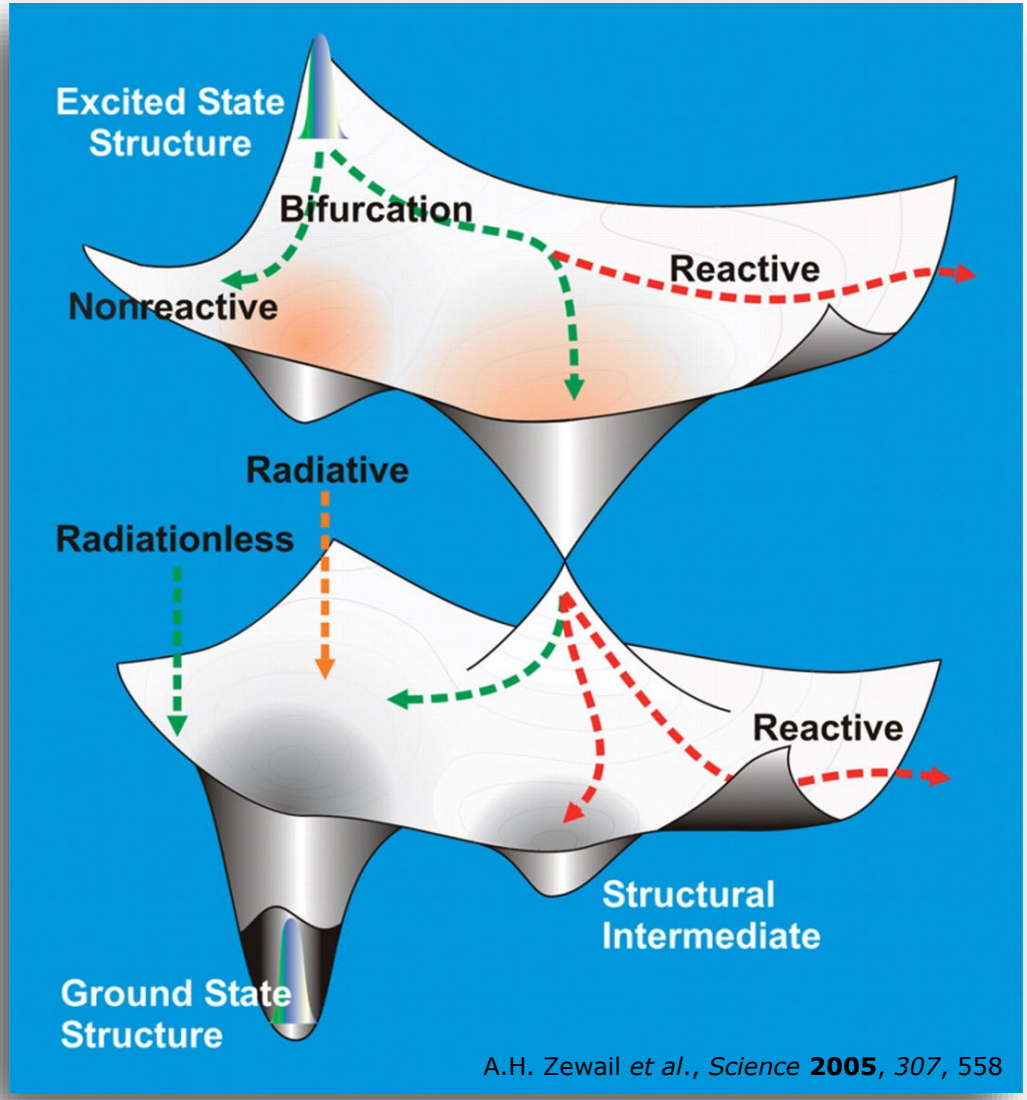
*Non-degenerate* potential energy surfaces

- *Barrier for crossing*
- *Rate dependent on barrier height*

*Degenerate* potential energy surfaces

- *Barrierless crossing*
- *Ultrafast rates*

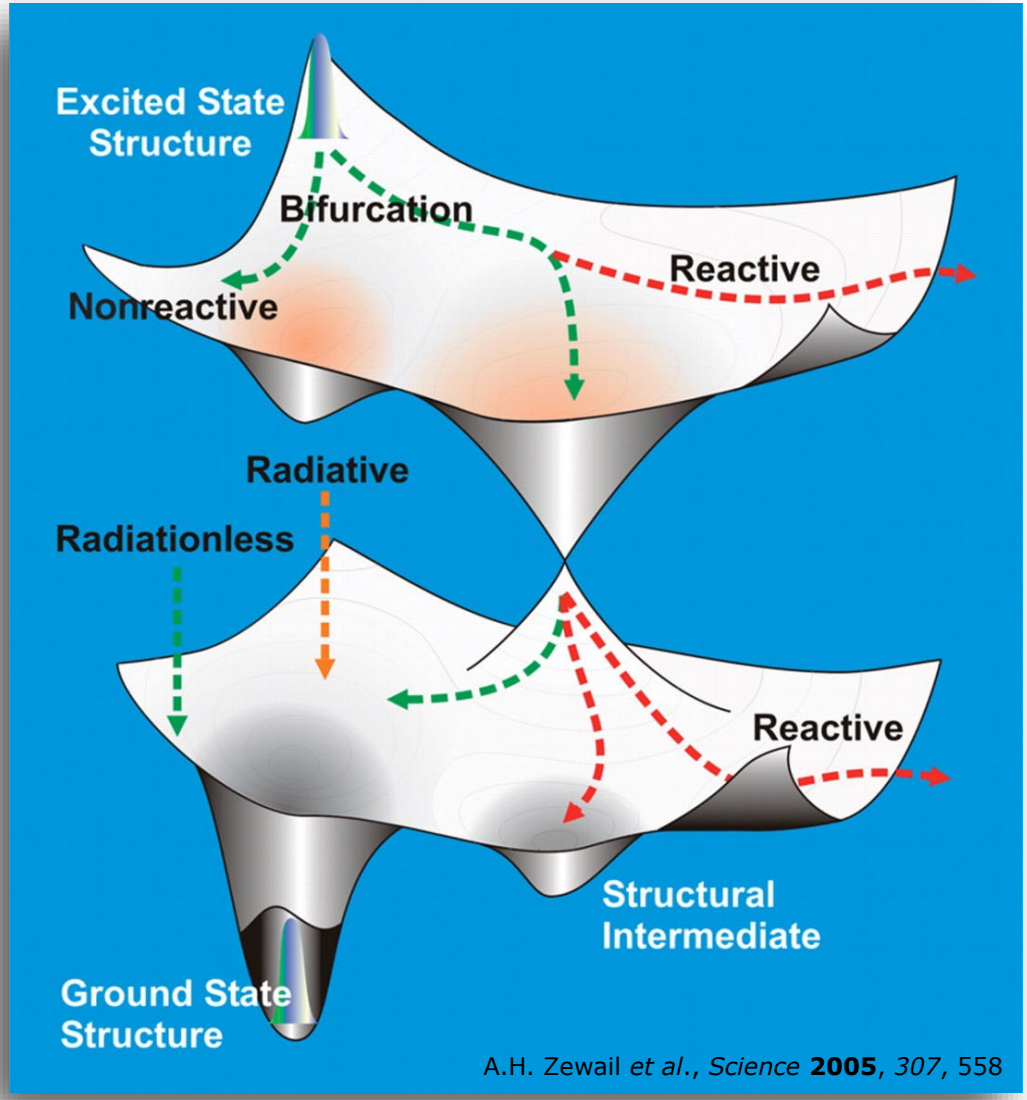
# The dark side of the force …




A.H. Zewail *et al.*, *Science* **2005**, *307*, 558

*"Once you start down the dark path, forever will it dominate your destiny, consume you it will"*

# Photons at work



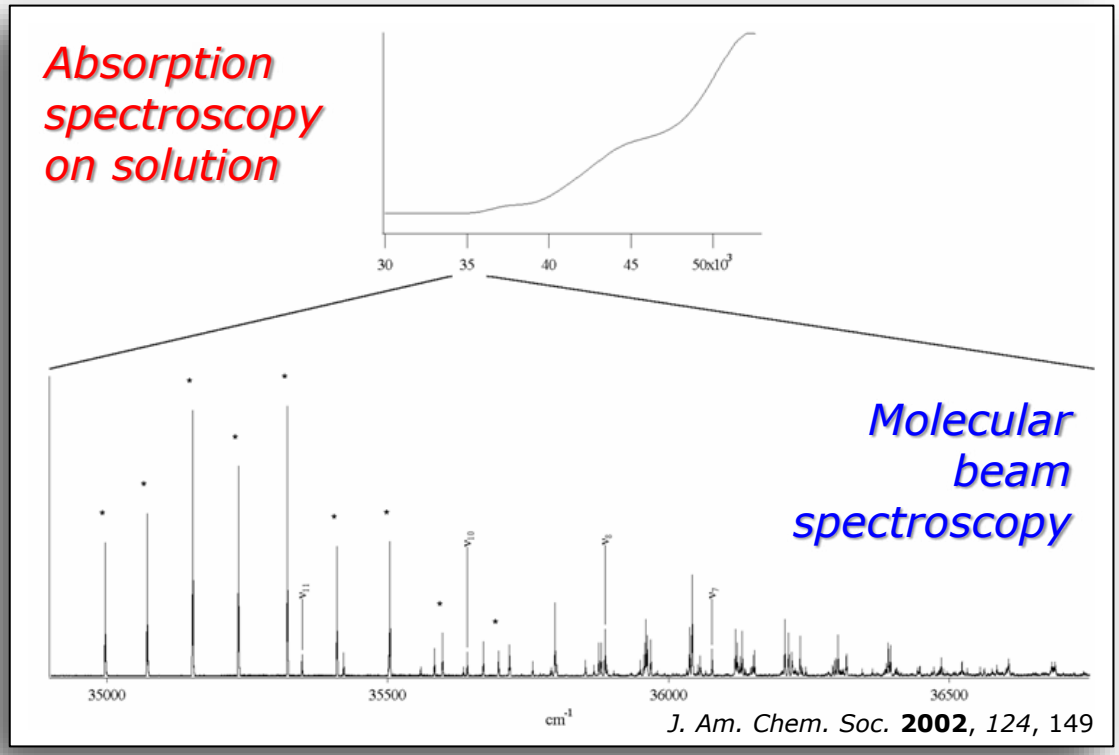

A.H. Zewail *et al.*, *Science* **2005**, *307*, 558

Light-to-activity path determined by potential energy surfaces electronically excited states

*Tailor photo(re)activity by fingerprinting potential energy surfaces using high-resolution spectroscopy*

# Fingerprinting potential energy surfaces

## Vibrational level structure gives access to

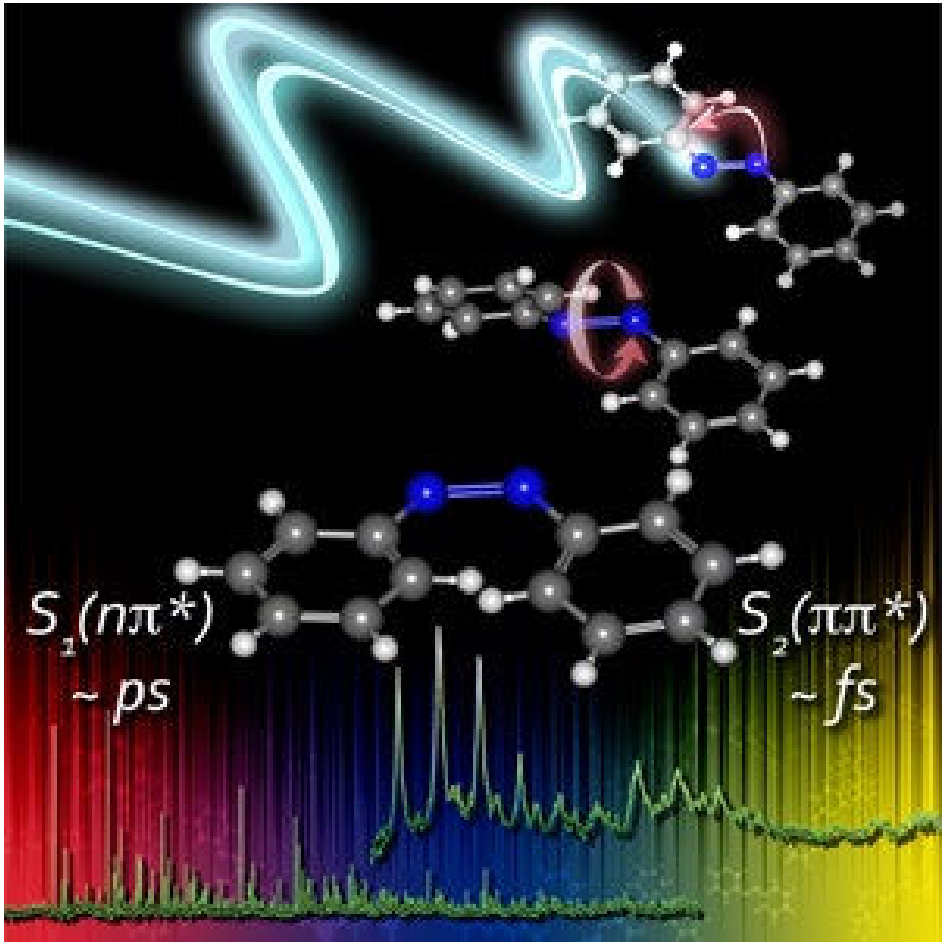



- *Forces on molecule after electronic excitation*
- *Changes in electronic and spatial structure*
- *Dynamics in electronically excited states*

# Scanning potential energy surfaces of azobenzene

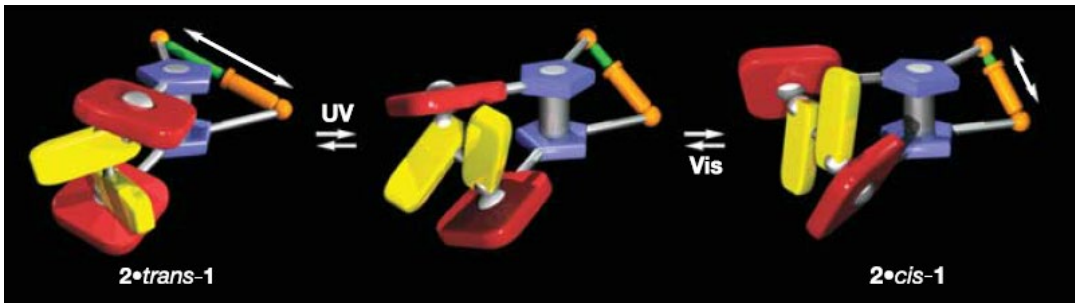
*Eric Tan*
*Saeed Amirjalayer*
*Szymon Smolarek*
*Alexander Vdovin*
*(University of Amsterdam)*

*Francesco Zerbetto*
*(Università di Bologna)*

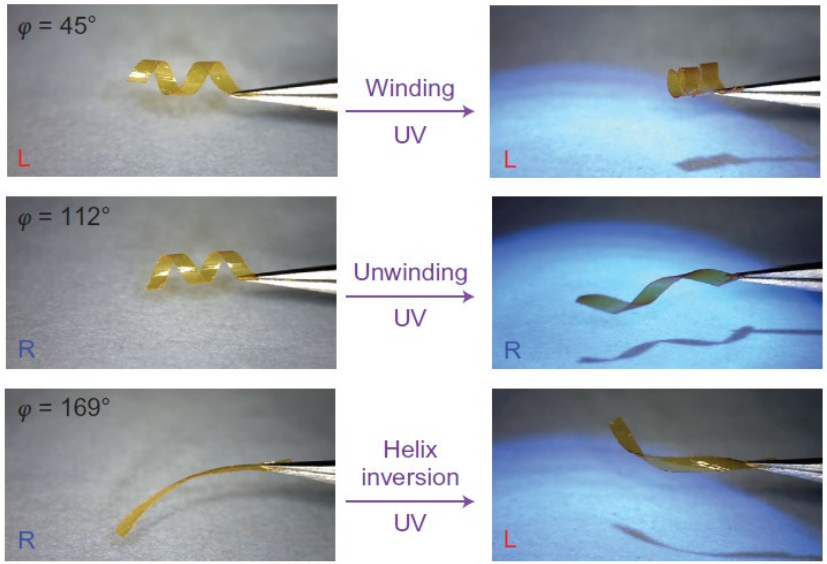


# Azobenzene at work …


*Angew. Chem. Int. Ed.* **2012**, *51*, 10500

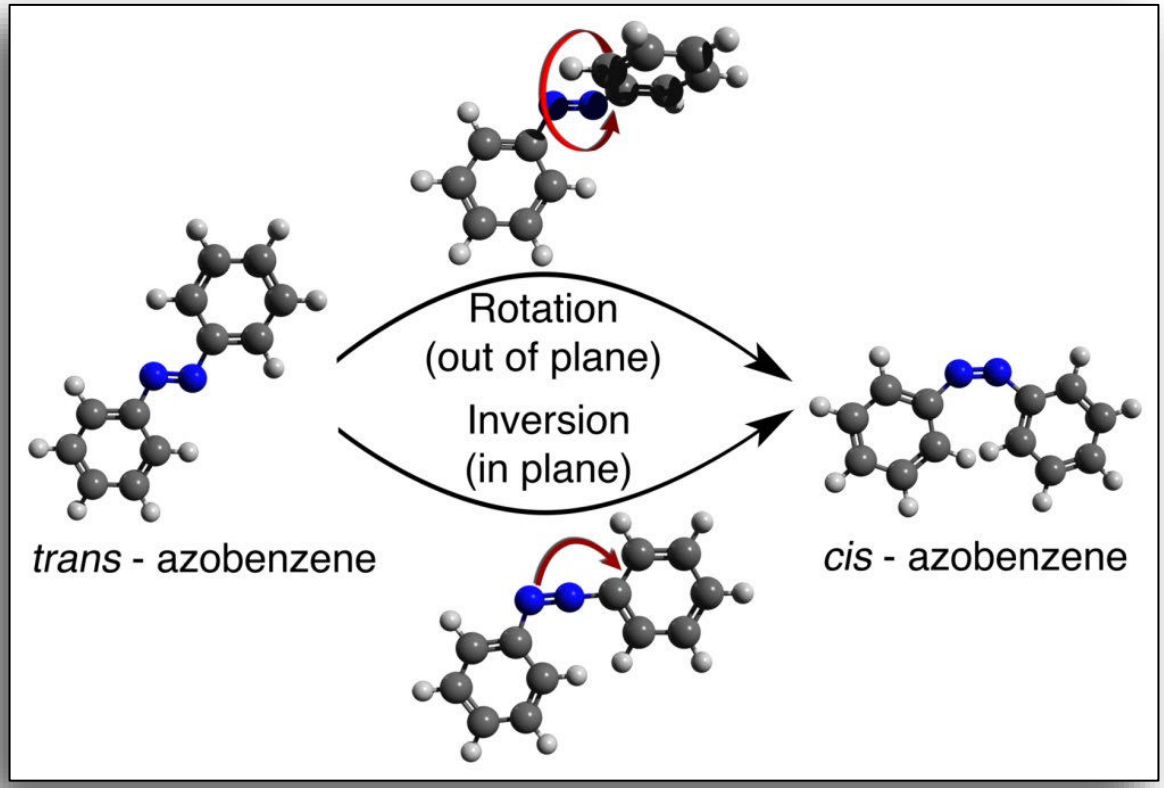



T.Muraoka, K. Kinbara, T. Aida, *Nature* **2006**, *440*, 512




N. Katsonis *et al.*, *Nat. Chem.* **2014**, *6*, 229

# … but how?

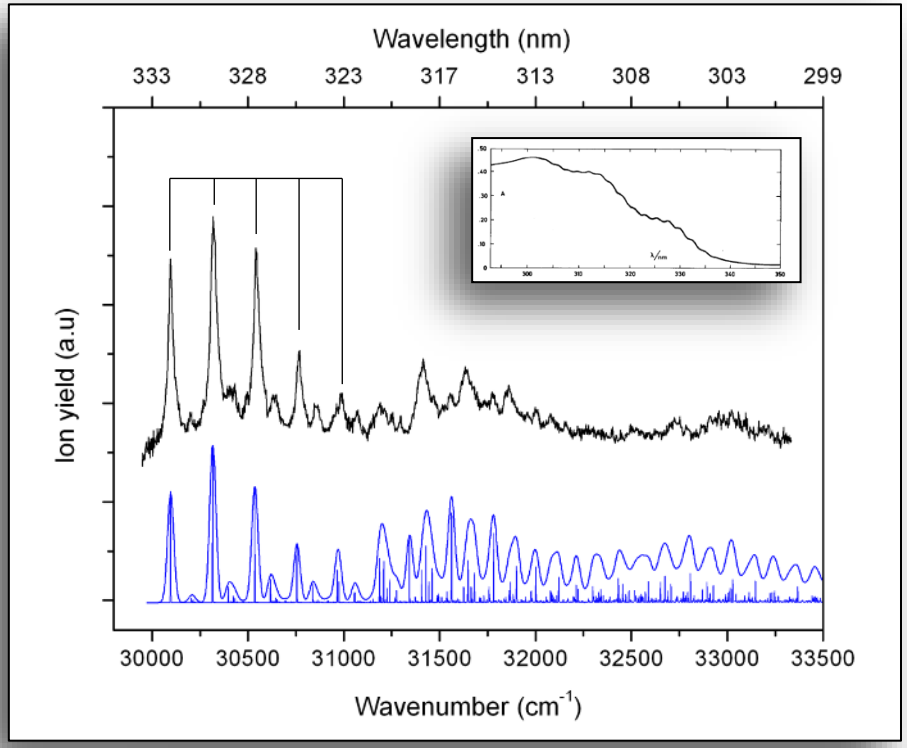



*Spectroscopic passport azobenzene*

Strongly allowed $S_2(\pi\pi^*)$ state

Forbidden $S_1(n\pi^*)$ state (*but here the action occurs* …)

# How to flash 170 fs with 10 ns:
## $S_2$ ($^1B_u(\pi\pi^*)$) ← $S_0$ excitation spectrum

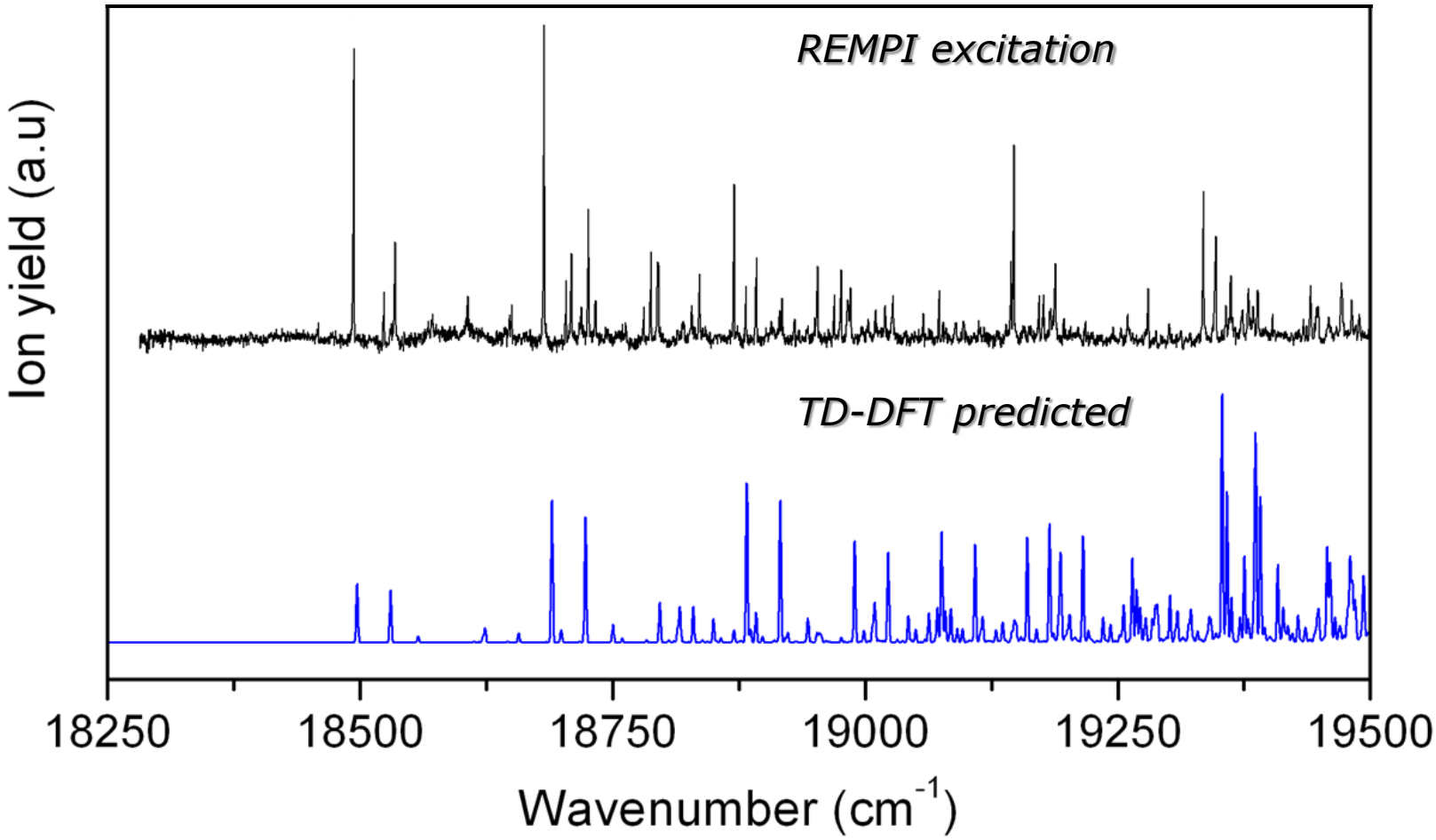



- Width (32 $cm^{-1}$) agrees with decay (170 fs) *internal conversion to $S_1(n\pi^*)$ dominates*
- Excellent agreement experiment and theory *molecular structure in $S_2(\pi\pi^*)$ determined*

| | $S_0$ (exp) | $S_2$ (calc) | $S_2$ (recon) |
|---|---|---|---|
| *d*(C-N) (Å) | 1.428 | 1.369 | 1.373 |
| *d*(N=N) (Å) | 1.260 | 1.351 | 1.324 |
| ∠N=N-C (°) | 113.7 | 111.5 | 112.2 |
| ∠C-C-N (°) | 124.8 | 124.4 | 124.6 |

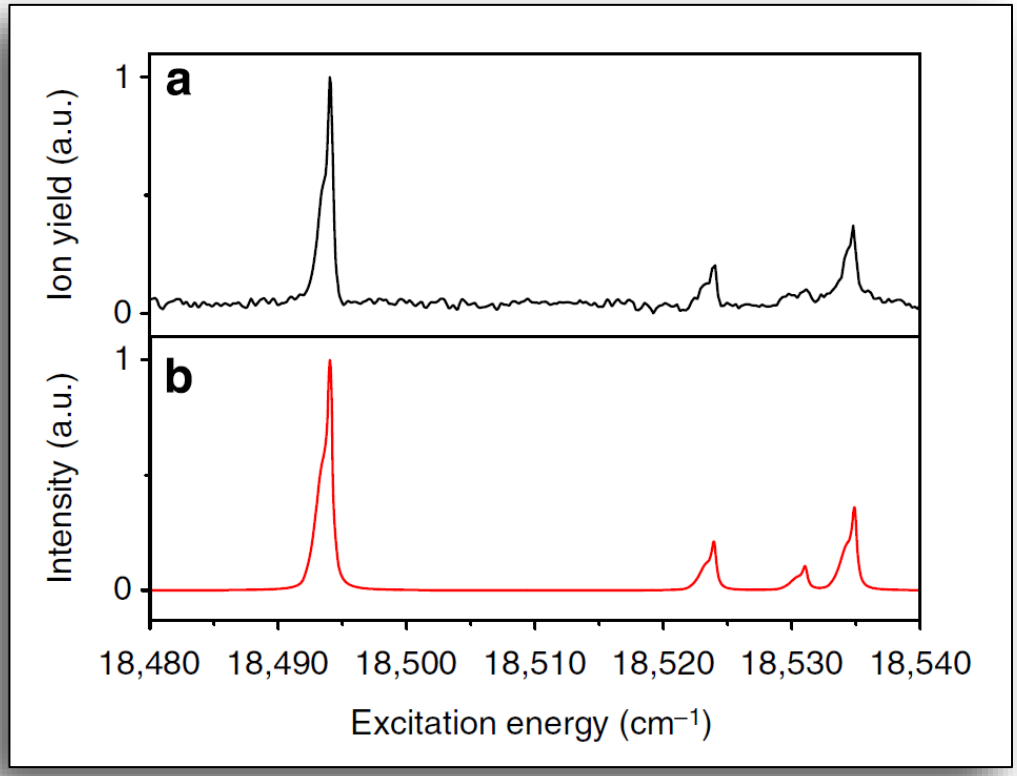
*Nat. Commun.* **2015**, *6*, 5860

# How to see the unobservable:
## $S_1$ ($^1B_g(n\pi^*)$) ← $S_0$ excitation spectrum




*Nat. Commun.* **2015**, *6*, 5860

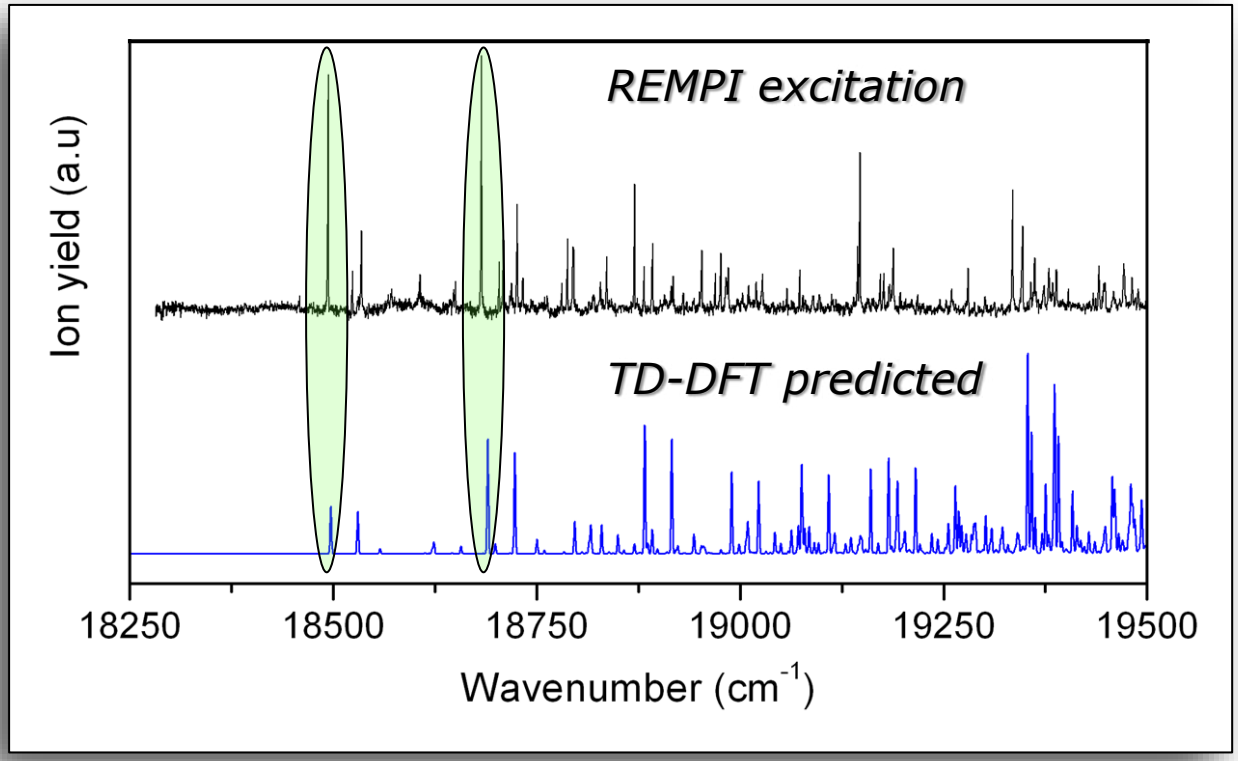
# Simulation rotational contours




Simulation:
- $T_{rot} \approx 9K$
- $^1B_u \leftarrow {}^1A_g$ transition
- homogeneous linewidth *0.4 cm$^{-1}$*

- $S_1$ ($^1B_g(n\pi^*)$) $\leftarrow$ $S_0$ transition vibronically induced via *$a_u$ coupling modes*
- *Lifetime ≈ 13 ps* order of magnitude longer than reported so far

# Changes in structure upon excitation



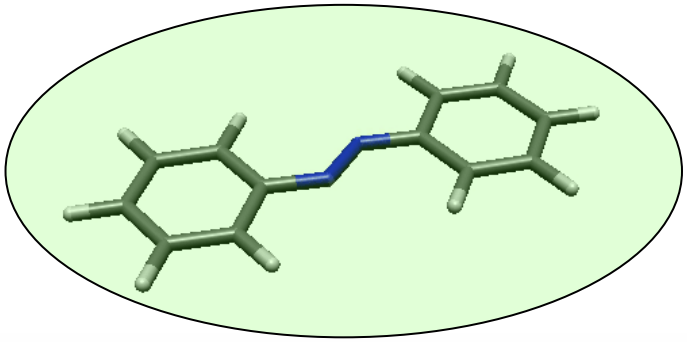

Reasonable agreement with predicted spectrum

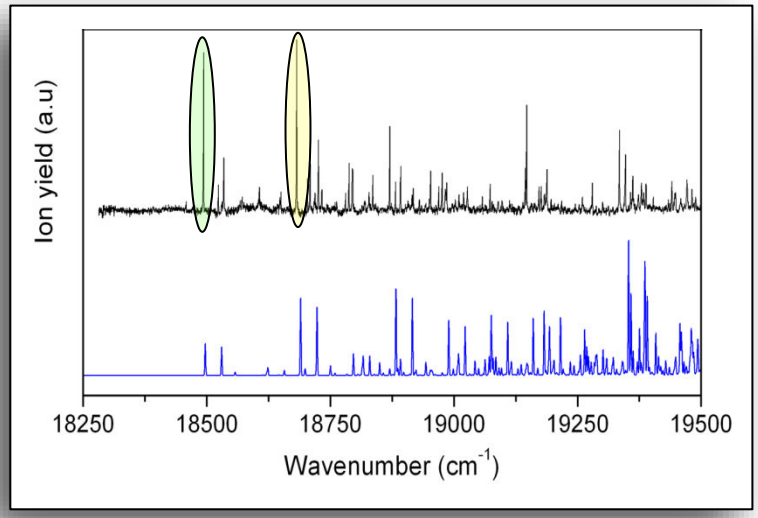
Calculations *overestimate changes inversion angle*

| | $S_0$ (exp) | $S_1$ (calc) | $S_1$ (recon) |
|---|---|---|---|
| *d*(C-N) (Å) | 1.428 | 1.358 | 1.365 |
| *d*(N=N) (Å) | 1.260 | 1.251 | 1.262 |
| **∠N=N-C (°)** | **113.7** | **130.5** | **124.3** |
| ∠C-C-N (°) | 124.8 | 122.2 | 123.3 |

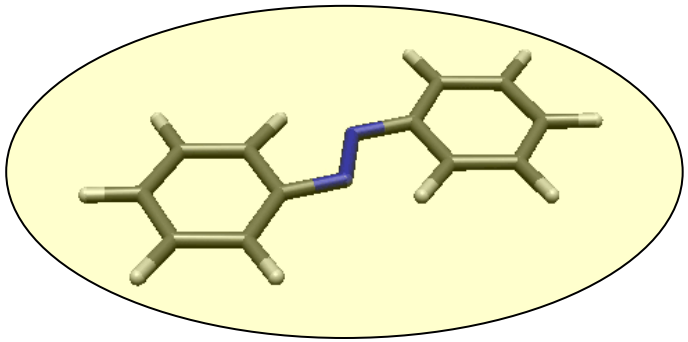
# Azobenzene isomerisation

*CNNC torsion* ($a_u$) *most effective in inducing transition to* $^1B_g(n\pi^*)$



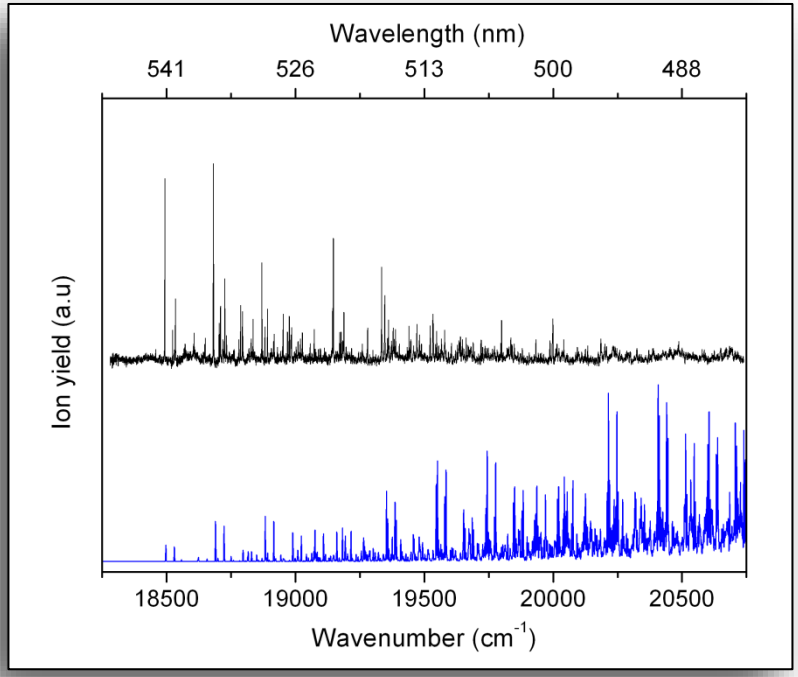


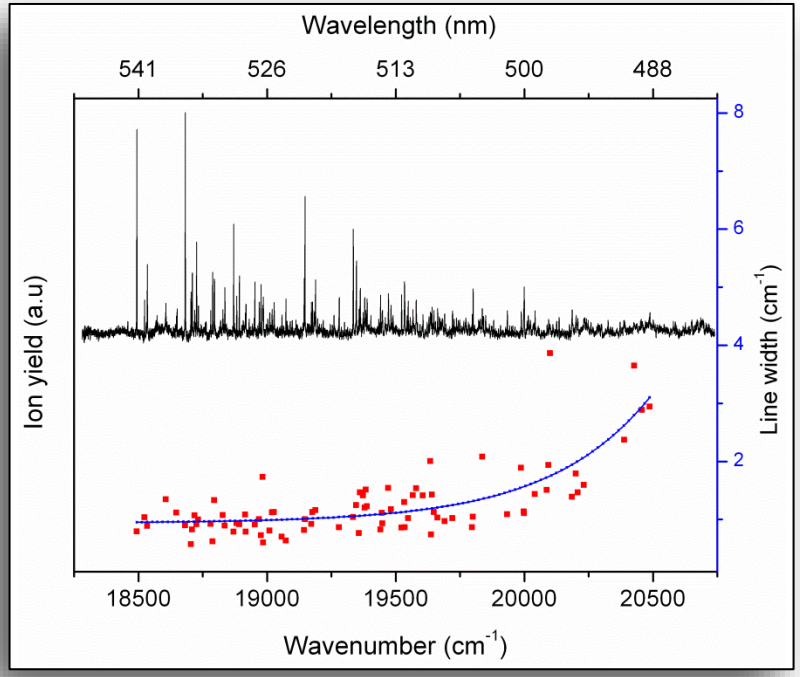

*Excitation induces large activity in-plane nitrogen inversion* ($a_g$)



Isomerisation proceeds along *inversion-assisted torsional pathway*

# Intensities and line widths




- Intensities in experimental and predicted spectrum start to deviate above ~19250 $cm^{-1}$
- Line width starts to increase above ~19250 $cm^{-1}$

*Barrier for isomerization ~2 kcal/mol in $S_1(n\pi^*)$*

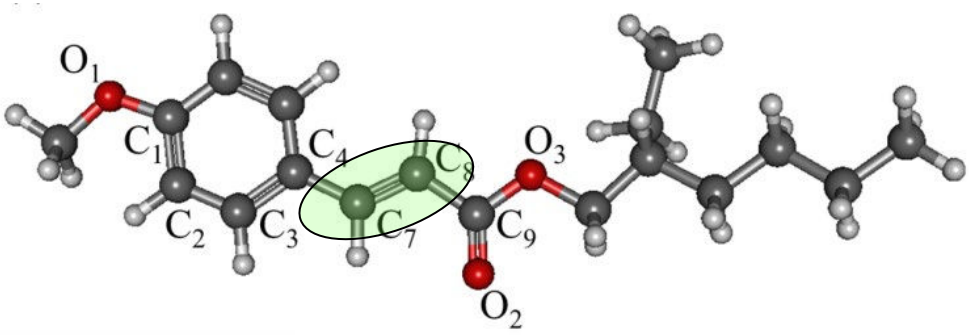
# Sunscreens

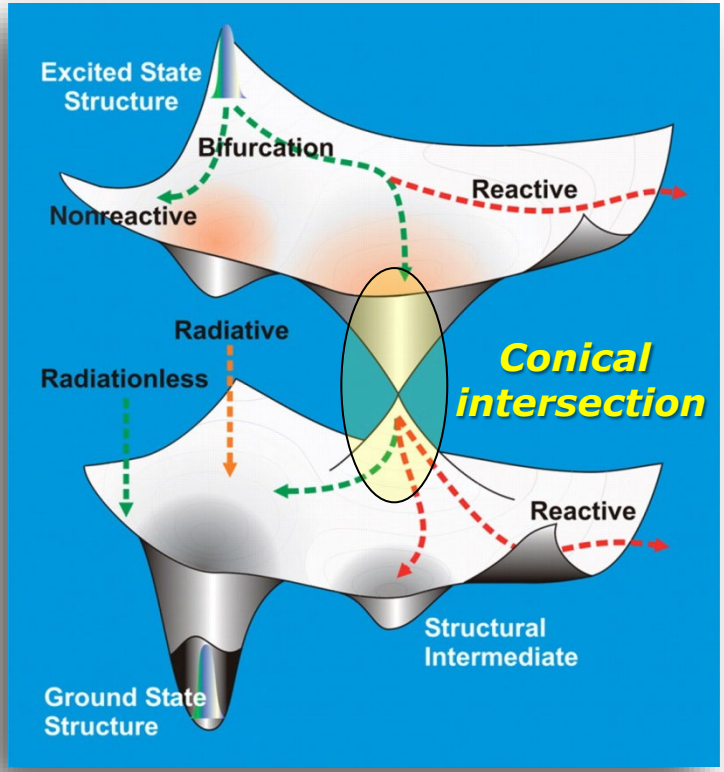
*Eric Tan*
*Mattijs de Groot*
*Szymon Smolarek*
*Michiel Hilbers*
*Alexander Vdovin*
*Saeed Amirjalayer*
*(UvA)*

*Marcel Drabbels*
*(EPFL)*

*Chris Bardeen*
*(UC Riverside)*

# The bright side of sunscreens




- 2-ethylhexyl-4-methoxycinnamate *UV-B filter*
- Fast *dissipation electronic energy* into heat by internal conversion through conical intersection

*Faraday Disc.* **2013**, *163*, 321

# The dark side of sunscreens

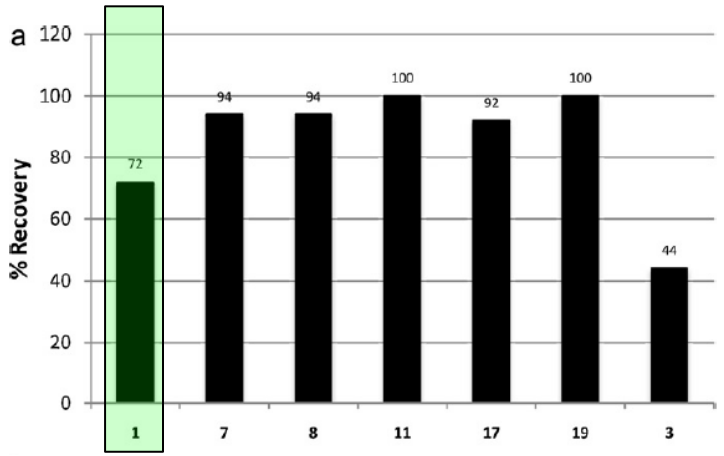
Mol Phot

## Sunscreen enhancement of UV-induced reactive oxygen species in the skin

Kerry M. Hanson [a,*], Enrico Gratton [b], Christopher J. Bardeen [a]

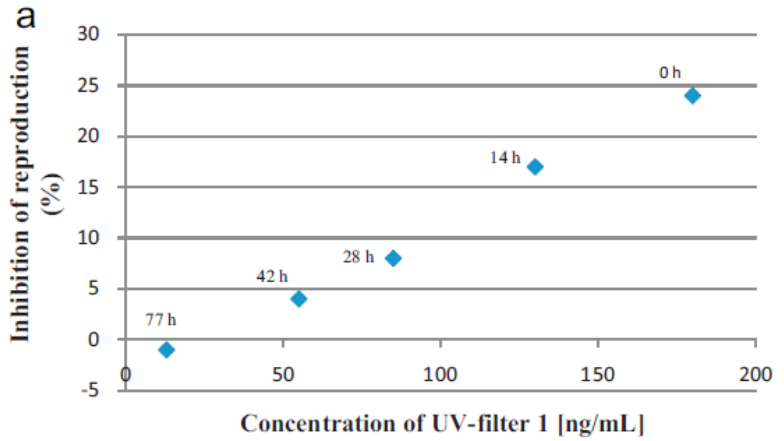
[a] *Department of Chemistry, University of California at Riverside, Riverside, CA 92506, USA*
[b] *Laboratory for Fluorescence Dynamics, Department of Bioengineering, University of California at Irvine, Irvine, CA 92697, USA*

## Recovery of UV-filters




*Degradation sunscreen*

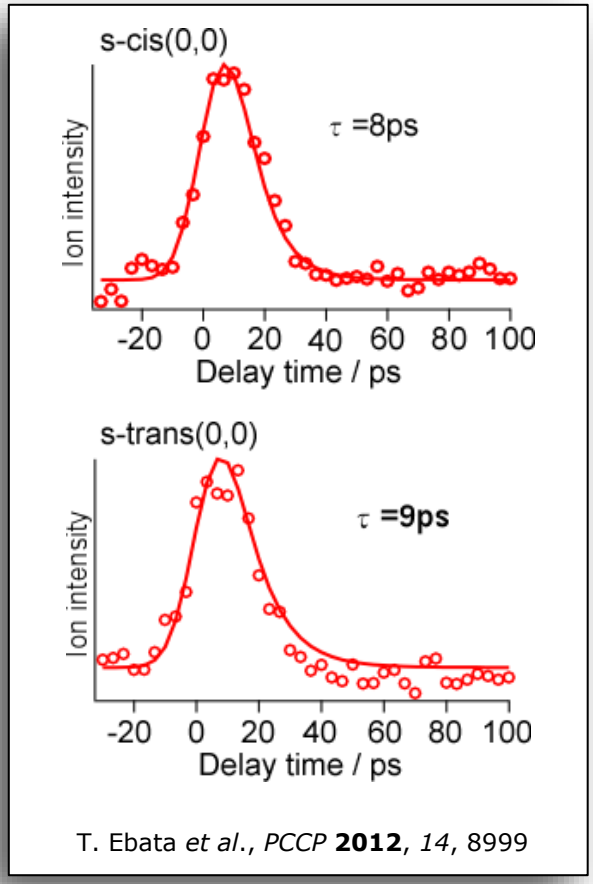
## Algal toxicity



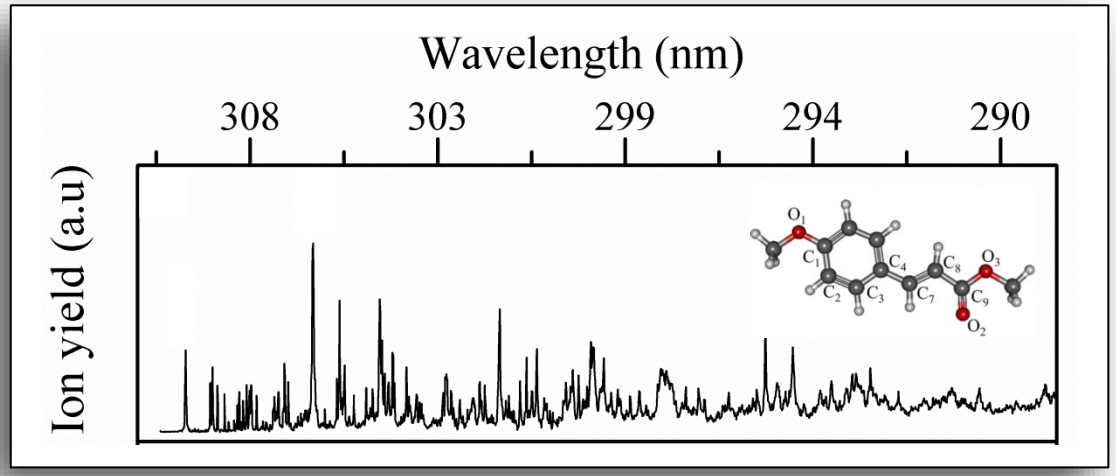

*Products less toxic than original sunscreen*

J. Kockler, M. Oelgemöller, S.Robertson, B.D. Glass, *J. Photochem. Photobiol. C* **2012**, *13*, 91

# Excited-state dynamics: the fast lane



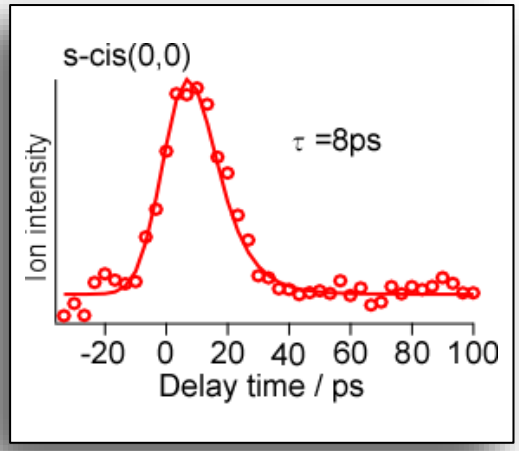

T. Ebata *et al.*, *PCCP* **2012**, *14*, 8999

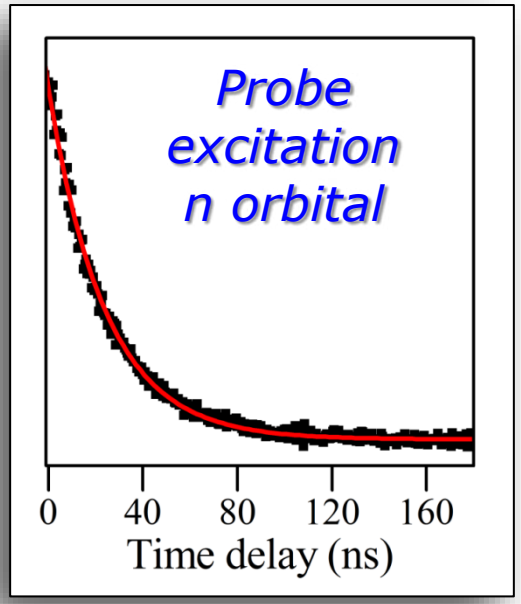



- Linewidth
  ~2-3 $cm^{-1}$ (2-3 ps decay)
- Time-resolved picosecond experiments show ps decay

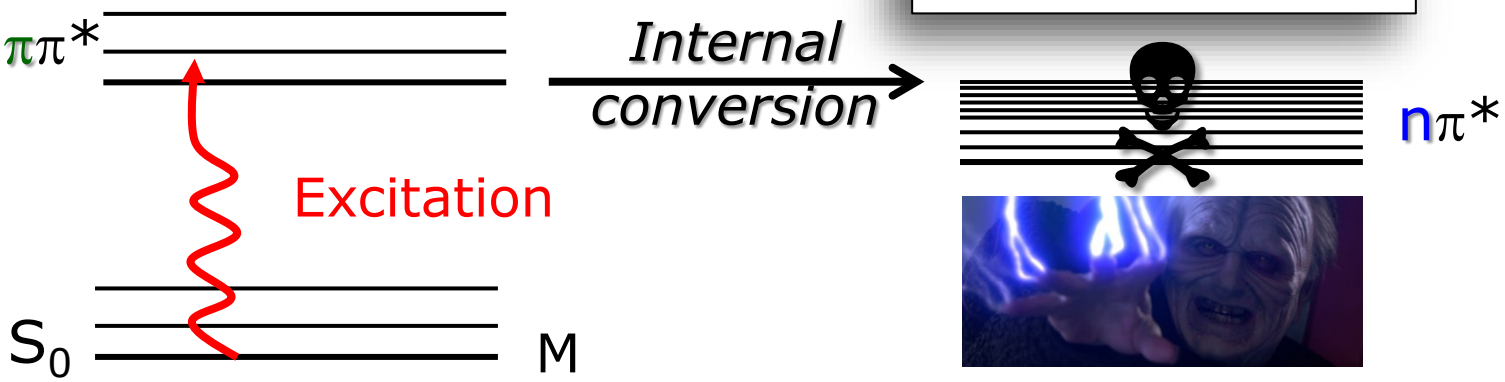
*JPC B* **2008**, *112*, 4427
*J. Am. Chem. Soc.* **2010**, *132*, 6315
*J. Phys. Chem. Letters* **2014**, *5*, 2464

# Fingerprinting dynamics by tracking ionization pathways



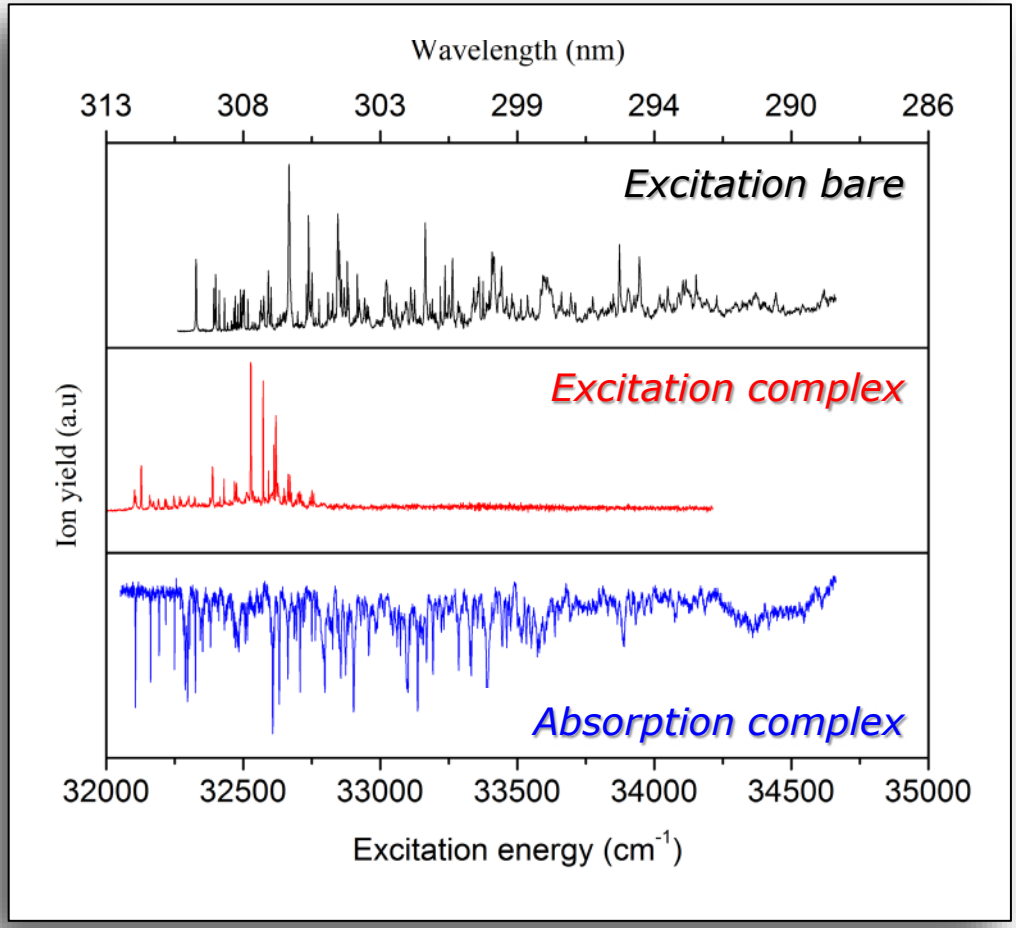




*Probe excitation π orbital*




*Proc. Nat. Acad. Sci. U.S.A.* **2009**, *106*, 2510
*J. Phys. Chem. Letters* **2014**, *5*, 2464

# From high-resolution spectroscopy to application




## *Water complexation*

- *removes bottleneck* (switch of ππ* and nπ* states)
- *improves performance* (lowers isomerization barrier)

**Improve sunscreens using reverse micelles**

*J. Phys. Chem. Letters* **2014**, *5*, 2464

# Conservation of misery at work

Mol Phot



PHOTOCHEMISTRY

## A bright future for sunscreens

Understanding the intrinsic properties of molecules that protect our skin from the harmful rays of the Sun is critical to developing more efficacious sunscreen products. Now, gas-phase spectroscopy and microsolvation studies of model ultraviolet-filter molecules have shown that they may provide a route to developing improved sunscreens.

Vasilios G. Stavros

Malignant melanoma is one of the most common cancers in the UK, with skin cancer incidence statistics showing around 13,000 new cases of malignant melanomas in 2011 (ref. 1). This alarmingly large number has meant that there have been increasing efforts towards developing more efficient sunscreens that act as ultraviolet light filters. Given their recognized importance and widespread commercial use, surprisingly little is known about how, after light absorption, these sunscreens disperse highly toxic UV energy in a non-toxic manner at the molecular level. Gleaning insight into such 'photoprotection' mechanisms will inevitably assist in developing next-generation sunscreens.

Now, writing in the *Journal of Physical Chemistry Letters*, Wybren Jan Buma and co-workers[2] show how the fundamental photochemical properties of common sunscreen constituents control their effectiveness as UV filters. Using gas-phase spectroscopy methods, which provide exquisite insight into the intrinsic properties of isolated molecules, they studied the initial molecule–photon interaction and tracked the subsequent photochemical 'cascade' — observing the behaviour of the molecule as it 'drops' from a high-energy excited state. They then demonstrate how the addition of just a single water solvent molecule (microsolvation) can dramatically alter the properties of sunscreen constituents. In doing so, they have taken a large step towards suggesting effective means by which to improve the efficacy of commercially available sunscreens.

Buma and co-workers chose to study 2-ethylhexyl-4-methoxycinnamate (EHMC), a molecule commonly used as a UV-B (315–280 nm) filter in sunscreens together with a simplified version of EHMC, methyl-4-methoxycinnamate (MMC). For both EHMC and MMC, absorption of a UV-B photon results in the promotion of an electron from a bonding $\pi$ orbital into an antibonding $\pi^*$ orbital, transforming both molecules into an excited singlet $\pi\pi^*$ state ($^1\pi\pi^*$). The frequency-resolved spectrum for this absorption process in MMC displayed a dense manifold of transitions to vibrational levels in the excited state, which they were able to attribute to two conformers — the *s-cis* (shown in Fig. 1) and *s-trans* conformers. Using these MMC studies as a benchmark, they were then able to assign the excitation spectrum for EHMC, once again to the *s-cis* and *s-trans* conformers. Most significantly though, the spectral linewidths from the excitation spectra provide information about the lifetimes of the states through the energy–time uncertainty principle, revealing picosecond lifetimes of the initially excited $^1\pi\pi^*$ states in both MMC and EHMC. However, this result appeared to be in stark contrast to their time-resolved measurements, which reported longer excited-state lifetimes on the order of nanoseconds.

The highly complementary frequency- and time-resolved studies enabled Buma and co-workers to propose that after excitation of a $^1\pi\pi^*$ state in MMC and EHMC, non-radiative internal conversion then causes transformation into a weakly absorbing (optically dark) excited $^1n\pi^*$ state, within a few picoseconds. It is this $^1n\pi^*$ state that is responsible for the longer nanosecond

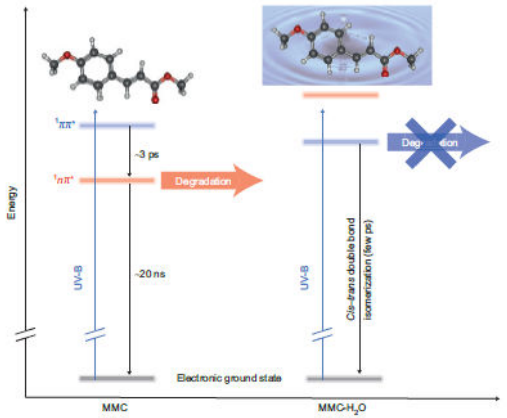



Figure 1 | A schematic of a proposed kinetic scheme for methyl-4-methoxycinnamate (MMC) and MMC-$H_2O$ following irradiation with UV-B. The addition of a water molecule reverses the energetic ordering of the $^1\pi\pi^*$ and $^1n\pi^*$ states shown in blue and red, respectively. In so doing, the $^1n\pi^*$ 'bottleneck' in MMC is removed. The photoexcited molecule can thus undergo much faster relaxation back to the electronic ground state, effectively bypassing photodegradation. Insets: molecular structure of *s-cis*-MMC (left) and 'microsolvated' *s-cis*-MMC (right). Figure reproduced with permission from ref. 2, © 2014 ACS; water ripple © PhotoDisc/Getty Images/Don Farrall.

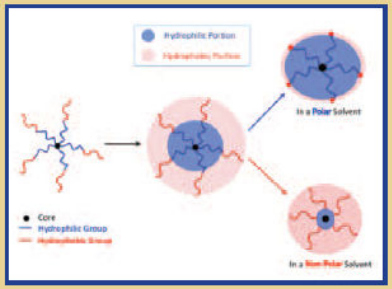




## SPIDER ESTERS®

URFA TECH

**Spider Esters®** are a class of patented[1-7] materials that were specifically designed to have a hydrophilic core surrounded by a hydrophobic periphery. This produces an amphillic polymer. Amphilic polymers contain two distinct regions that have different polarities covalently bonded together. This amphilic nature makes spider esters very attractive because of their unique solubilites. Amphilic polymers are covalently bonded together and do not have the same inherent stability issues that are evident in emulsions. Oil in water emulsions have pockets of hydrophobic oil contained in the core of micelles surrounded by an aqueous environment. When hydrophobic organic sunscreens are added into the emulsion, they migrate into the hydrophobic micelle cores and remain suspended in a unified matrix. When the **Spider Ester** is introduced into a polar solvent, the hydrophobic periphery will collapse upon itself to minimize its contact with the solvent environment.




The dual polarities of **Spider Esters®** make them soluble and effective when added into polar oil based sun care formulations as well as non-polar oil based sunscreen formulations. The major benefit of these **Spider Esters** is that they are capable of "encapsulating" sunscreen filters in the core and "shielding" them from the surrounding environment. This allows the filters to be placed into a wide variety of solvents, also this "shielding" of the filters can drastically improve their performance. The hydrophilic core will respond to the polar solvent in the opposite manor, the solvent will cause the core to swell and maximize its contact with the polar solvent. This phenomenon is the basis for the "loading" or encapsulation of small molecules into the core of the **Spider Ester**. We have coined this phenomenon the "Spider Effect".

### SPIDER STRUCTURE

### SPIDER ESTER SOLUBILITY

**Spider Esters** have solubility in a wide variety of solvents.

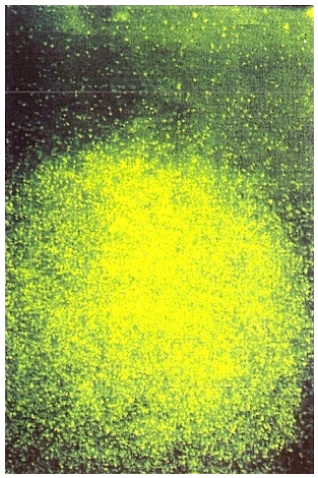
| Solvent (10 wt %) | Spider Ester® ESO | Spider Ester® GEC |
|---|---|---|
| Water | Milky | Milky |
| Propylene Glycol | Translucent | Translucent |
| Isopropanol | Soluble | Soluble |
| Sorbitol | Translucent | Soluble |
| Cyclomethicone | Translucent | Translucent |
| Sunflower Oil | Soluble | Soluble |
| Isododecane | Soluble | Soluble |

**Spider Esters** solubilize a variety of actives including:

- Sunscreen actives
- Enzymes
- Benzoyl Peroxide (BPO)
- DHA
- Drugs
- Antioxidants
- Salicylic Acid
- Vitamins
- Peptides

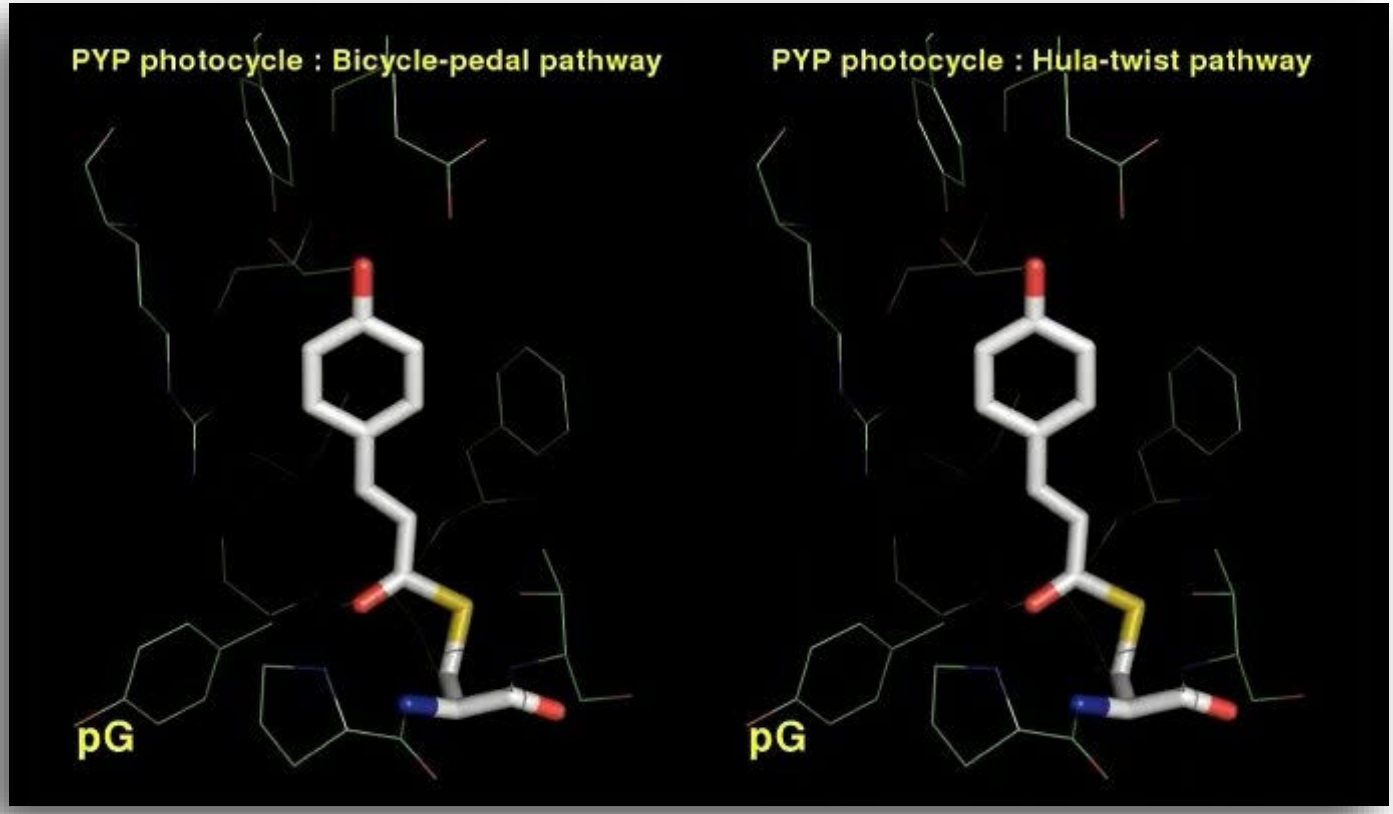
# How nature optimizes: sunscreens with benefits

Mol Phot



W.W. Sprenger *et al.*, *J. Bacteriol.* **2008**, 175, 3096

## Bacterial phototaxis
## *e.g.* in *Extothiorhodospira halophila*




Y.O. Jung *et al.*, *Nat. Chem.* **2013**, *5*, 212

# Rational design of sunscreens

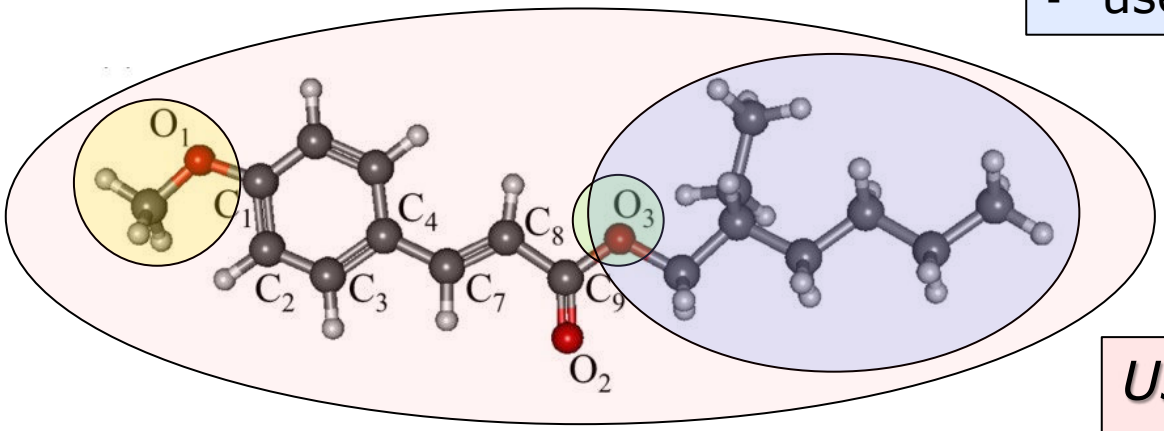
Mol Phot

***Replace by OH and deprotonate***

- nπ* to much higher energies
- V(bonding MO → anti-bonding MO) lowest ππ* state
- V(ππ*) isolated from other states

***Couple to protein backbone***

- enable photocycle
- use photon energy for motion



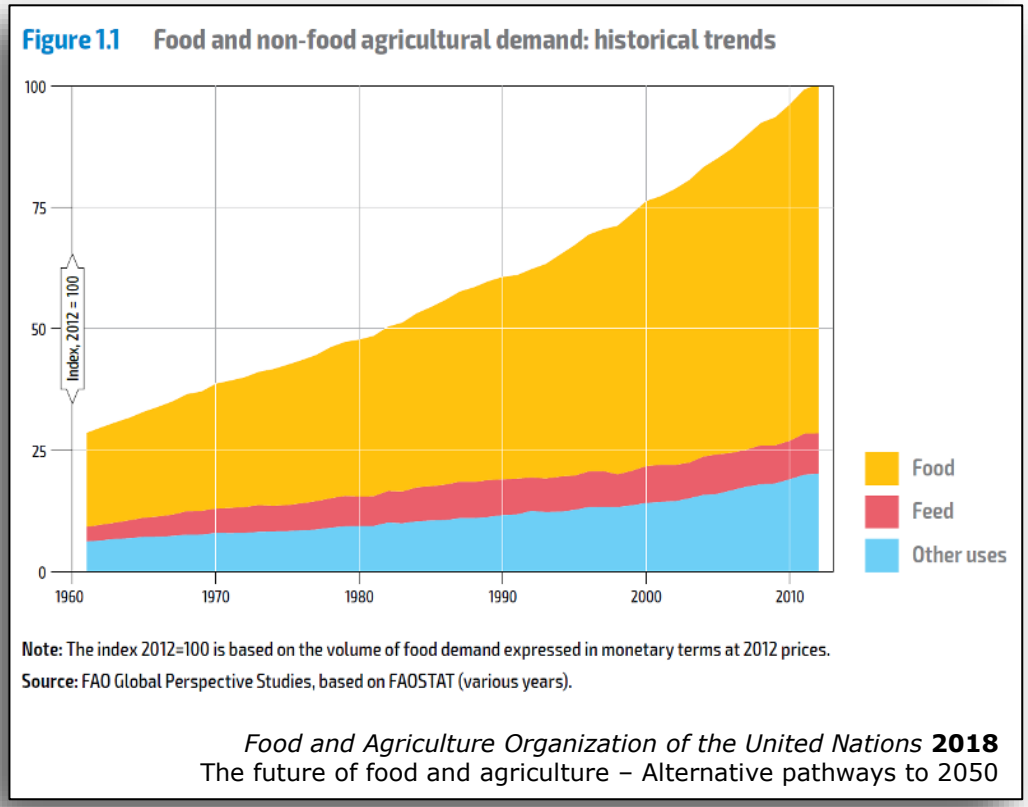

***Replace O by S***

- red shift of V(ππ*) state
- additional blue shift nπ* state

***Use interactions with environment***

- tune absorption maximum *(ΔE at $S_0$ geometry)*
- tune $S_1$-$S_0$ energy gap *(ΔE at $S_1$ geometry)*

# Food Security




Projected food demand:

***double global crop production needed by 2050***

- Increase *crop yields*
  - *extend growth season*
  - *grow at high crop densities*
- Increase *arable land*
  - *cold stress tolerance*
  - *higher altitudes*

# Molecular heaters to boost crop yields

Mol Phot

Convert *photon energy* into *temperature increase*

## Wish list

- Absorption at wavelengths harmful to plants (UV) or not used in photosynthesis (Red/Far-Red)
- Use *natural photoprotective molecules*
- Maximize photon-to-heat conversion yield
- Temperature increase ~3°C

## Benefits

- Protection against harmful UV
  *agriculture at higher altitudes*
- Reduction shade avoidance
  *higher crop densities*
- Minimize toxicity and detrimental side reactions
- Temperature increase
  *avoid cold stress*
  *anticipate growth season*
  *reduce energy costs*

# FET-Open
# BoostCrop consortium


University of Warwick (UK)

University of Bristol (UK)

University of Amsterdam (NL)

Radboud University (NL)

AgroParisTech (F)

Université d'Aix Marseille (F)

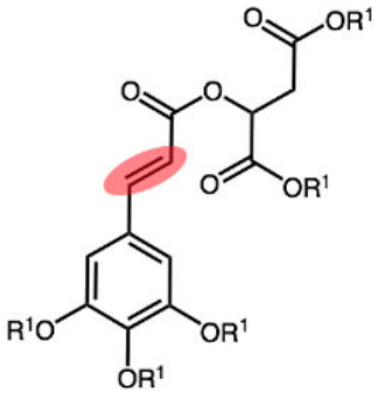
Bundesinstitut für Risikobewertung (D)

Plantresponse Biotech SL (ES)

# Boostcrop@Warwick (pre-corona)

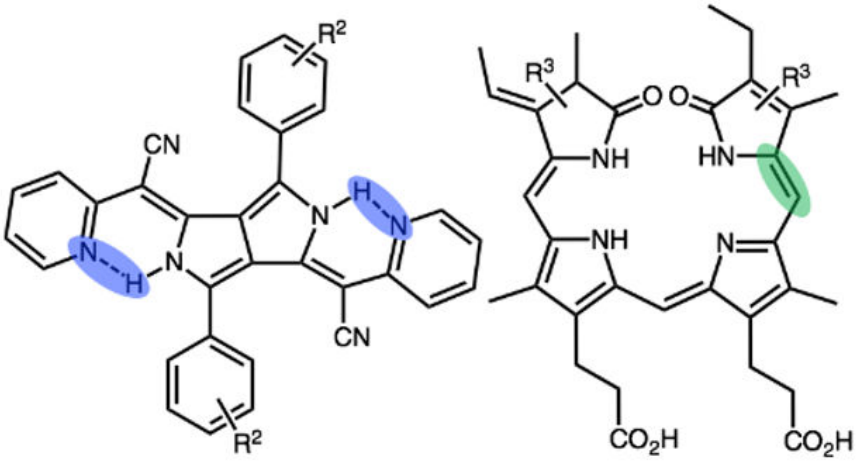

Nadav Joosten (BSc); Myrthe Praat, Yorrick Boeije, Laura Finazzi (MSc)
Dr. Wim Roeterdink; Ing. Michiel Hilbers

# Target chromophores



## Sinapate esters

- *Sinapoyl malate UV-B screening agent in plants*
- *Ultrafast relaxation due to conical intersection along isomerisation coordinate*



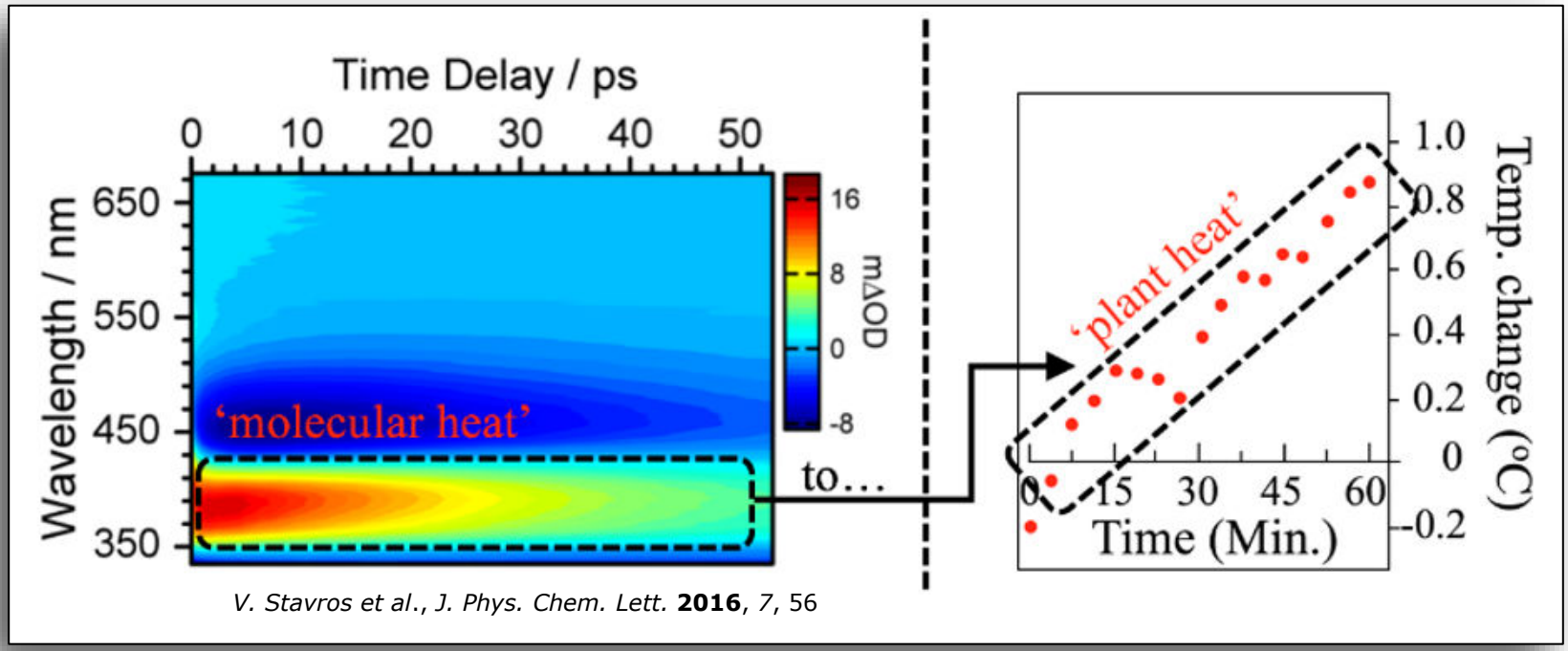
## Diketopyrrolopyrroles

- *R/FR dyes*
- *Large-amplitude motions induce non-radiative decay*

## Phytochromes

- *Plant R/FR photoreceptor*
- *Isomerisation methine bridge leads to ultrafast relaxation*

# Proof-of-principle: temperature increase

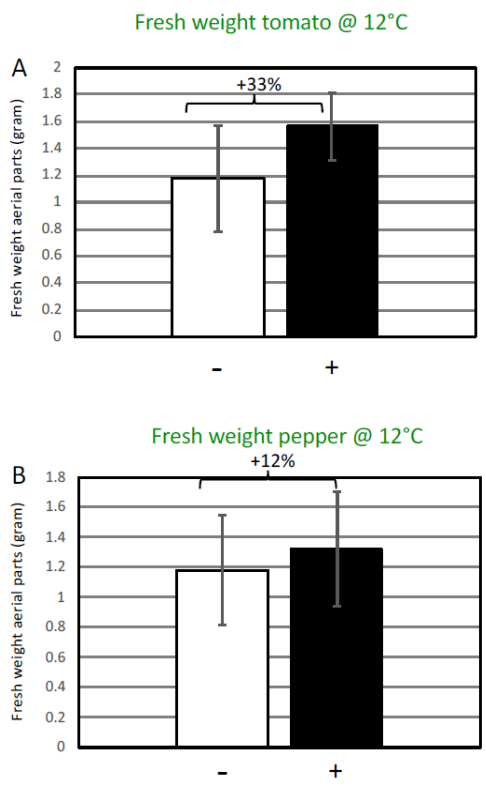



*V. Stavros et al., J. Phys. Chem. Lett.* **2016**, *7*, 56

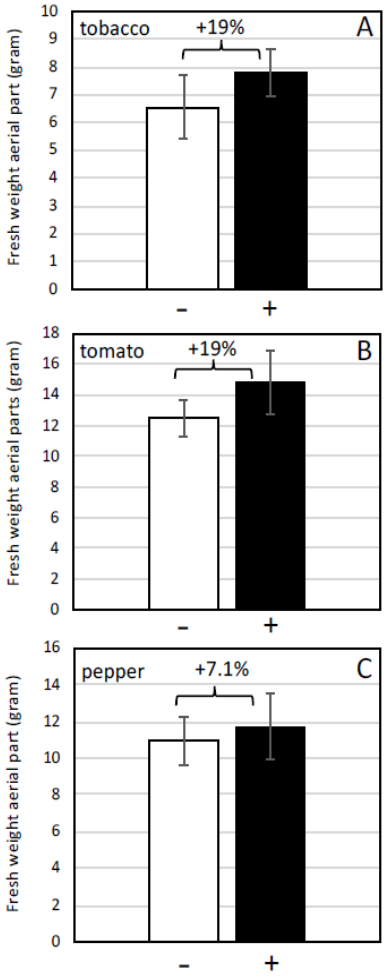
- *Tobacco leaves sprayed with 10 mM sinapoyl malate solution*
- *Ambient typical Bristol cloudy-day conditions*
- *Monitoring temperature using thermal imaging*

# (Possible) proof-of-principle: increase biomass

## *Low-temperature (12°C) conditions*




## *Ambient greenhouse conditions*



# Optimization molecular heaters: spectroscopy and dynamics

Mol Phot

## Spectroscopy cinnamates

- Determined by three close-lying states (V($\pi\pi^*$), V'($\pi\pi^*$) and n$\pi^*$)
- Dependence properties on *substitutions* and *conformational structure*
- Influence solvent

## Dynamics cinnamates

- Optimization *productive* nonradiative pathways
- Presence of *detrimental* decay pathways
- Excitation energy dependence

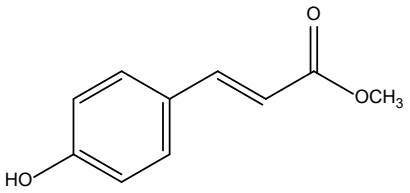
## Alternative natural sunscreens

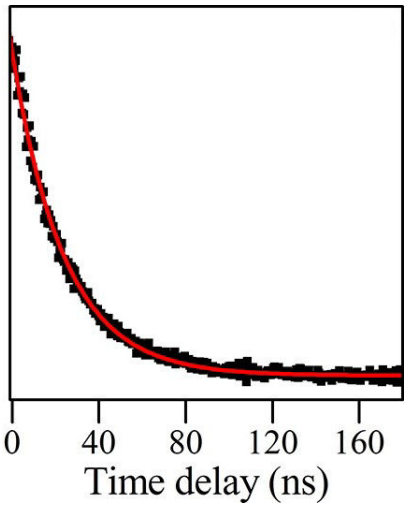
- *Tailoring absorption spectrum* to solar spectrum and photosynthesis

# Harmful energy dissipation pathways

Mol Phot

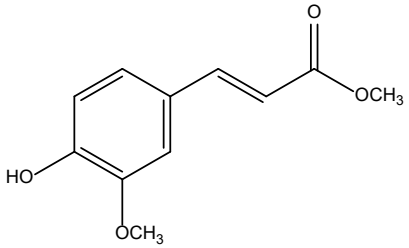
## Methylcoumarate

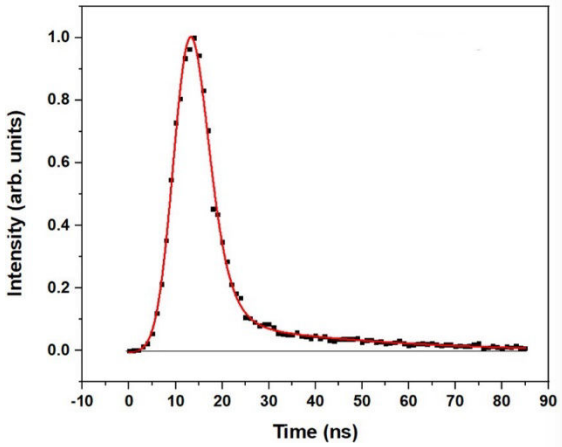



$\tau_1$=31 ns (1.00)

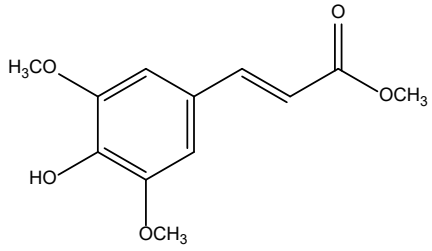
## Methylfumarate

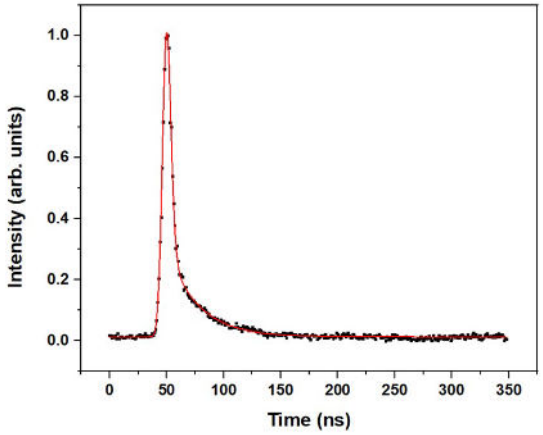



$\tau_1$=3 ns (0.90)
$\tau_1$=35 ns (0.10)

## Methylsinapate



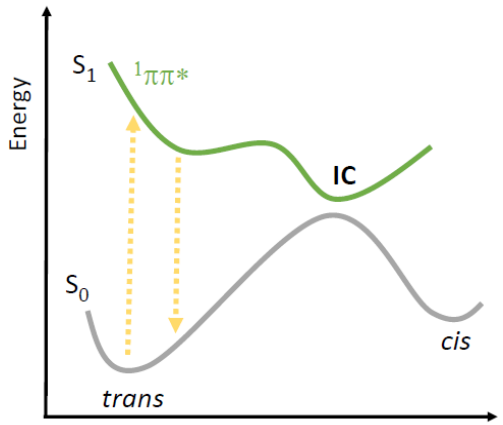




$\tau_1$=2 ns (0.93)
$\tau_1$=27 ns (0.07)

*Mol. Phys.* **2021**, *119*, e1825850; *Phys. Chem. Chem. Phys.* **2022**, *24*, 3984; *I. Romanov, Y. Boeije et al., to be submitted*

# Energy conversion pathways

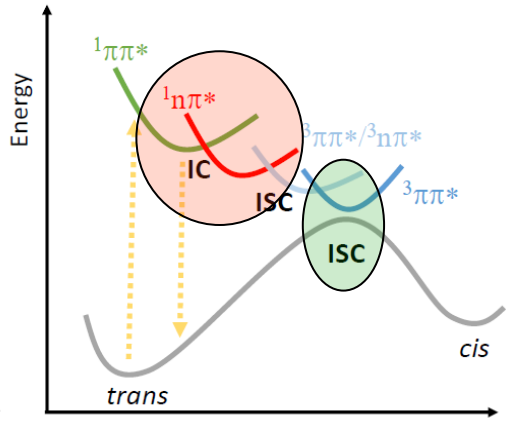
## *Fast dissipation*



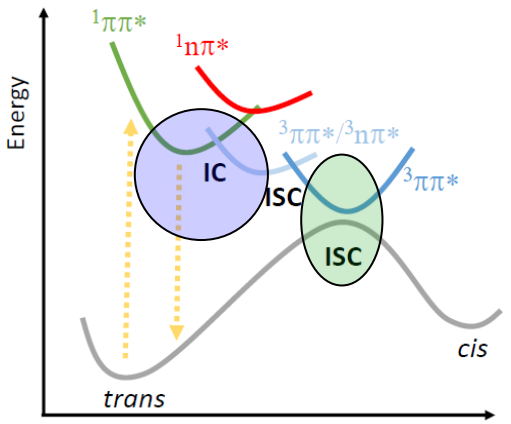

CI $S_1/S_0$ leads to ultrafast dissipation

*ideally low photo-isomerization quantum yield*

## *Fast slow decay*




## *Slow slow decay*




Fast internal conversion $^1\pi\pi^* \rightarrow {}^1n\pi^*$

*only possible in coumarates*

$k_{ISC}$ $^1n\pi^* \rightarrow {}^3\pi\pi^* \gg {}^1\pi\pi^* \rightarrow {}^3\pi\pi^*$

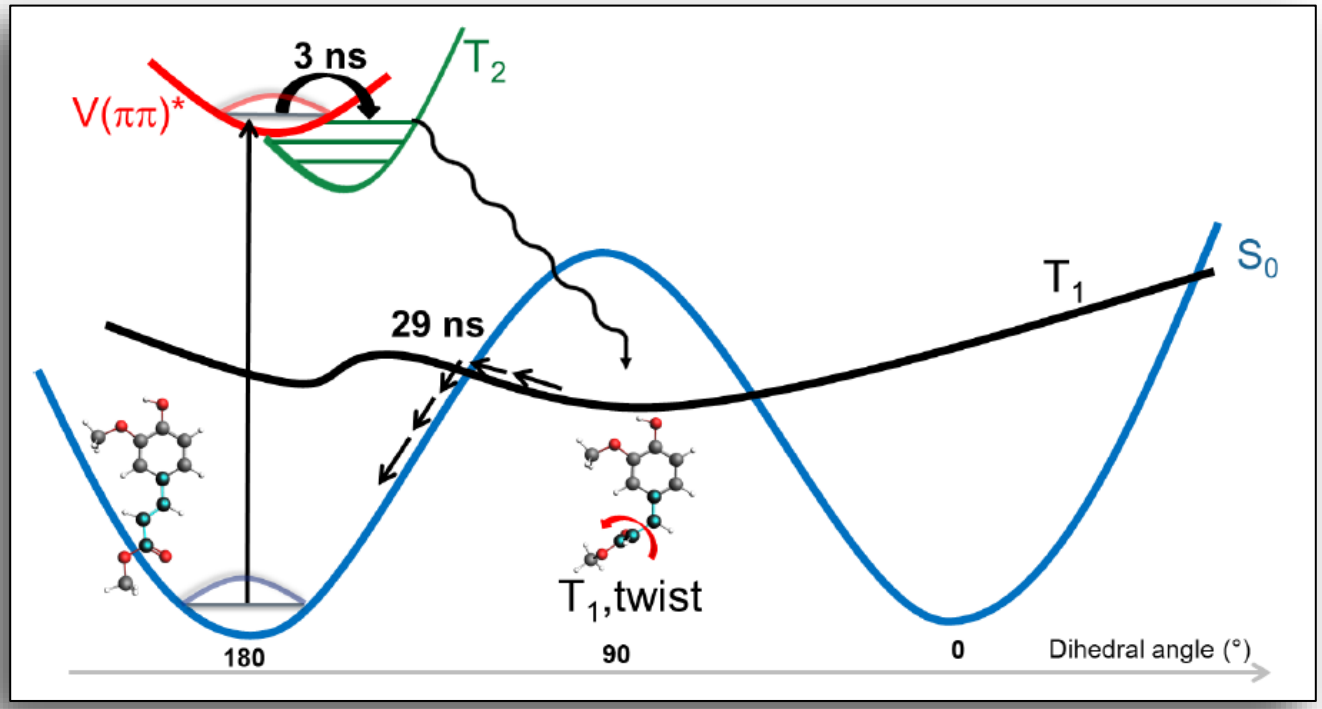
*slow ISC in fumarates and sinapates*

$S_0/T_1$ crossing leads to ns triplet decay

*universal feature in all chromophores*

*Diagrams courtesy M. Barbatti*

# Triplet-mediated photon-energy conversion pathway

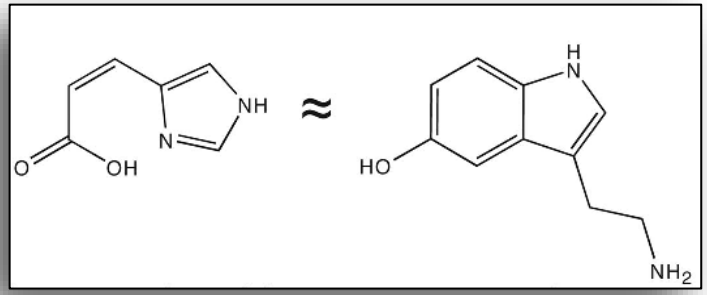


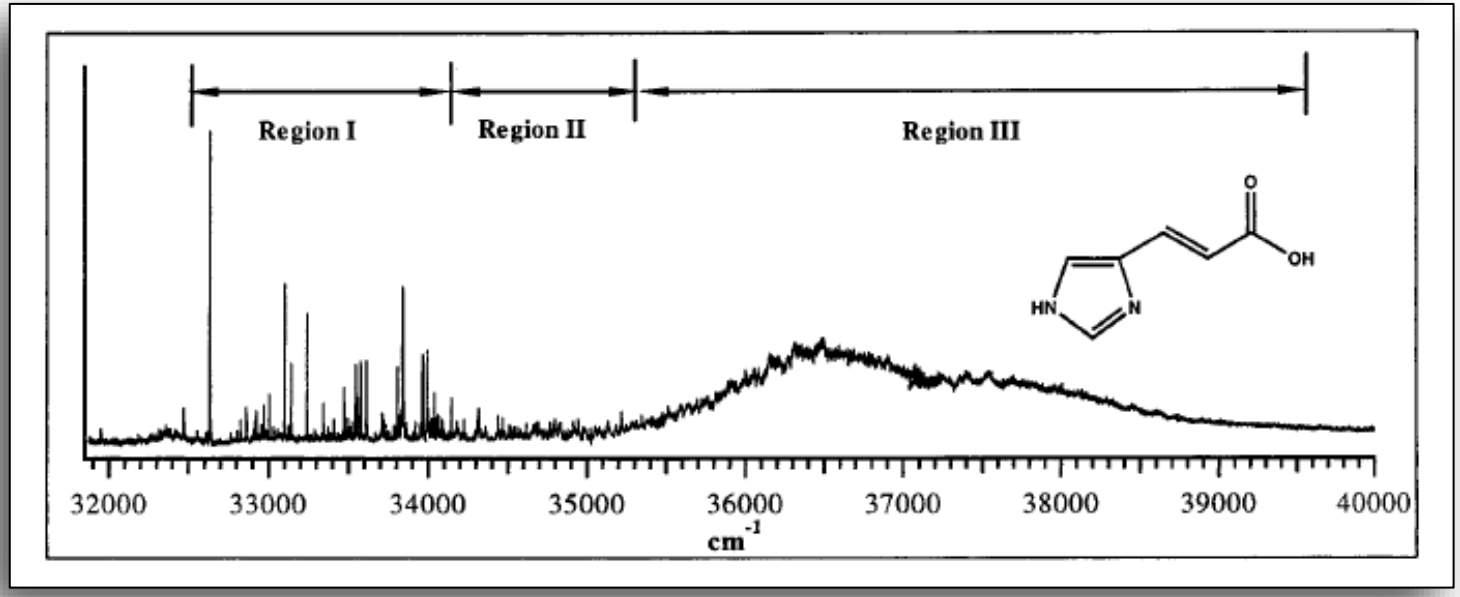

- *Perpendicular geometry* $T_1(\pi\pi^*)$ leads to $S_0/T_1$ crossing
- Crossing not sensitive to details phenyl substitution → *similar lifetimes*

*I. Romanov, Y. Boeije et al., to be submitted*

# Urocanic acid based chromophores

- Natural UV-A/B sunscreen present in skin
- Cis-isomer immunosuppressive serotonin receptor agonist
- Substitution might avoid agonistic effects

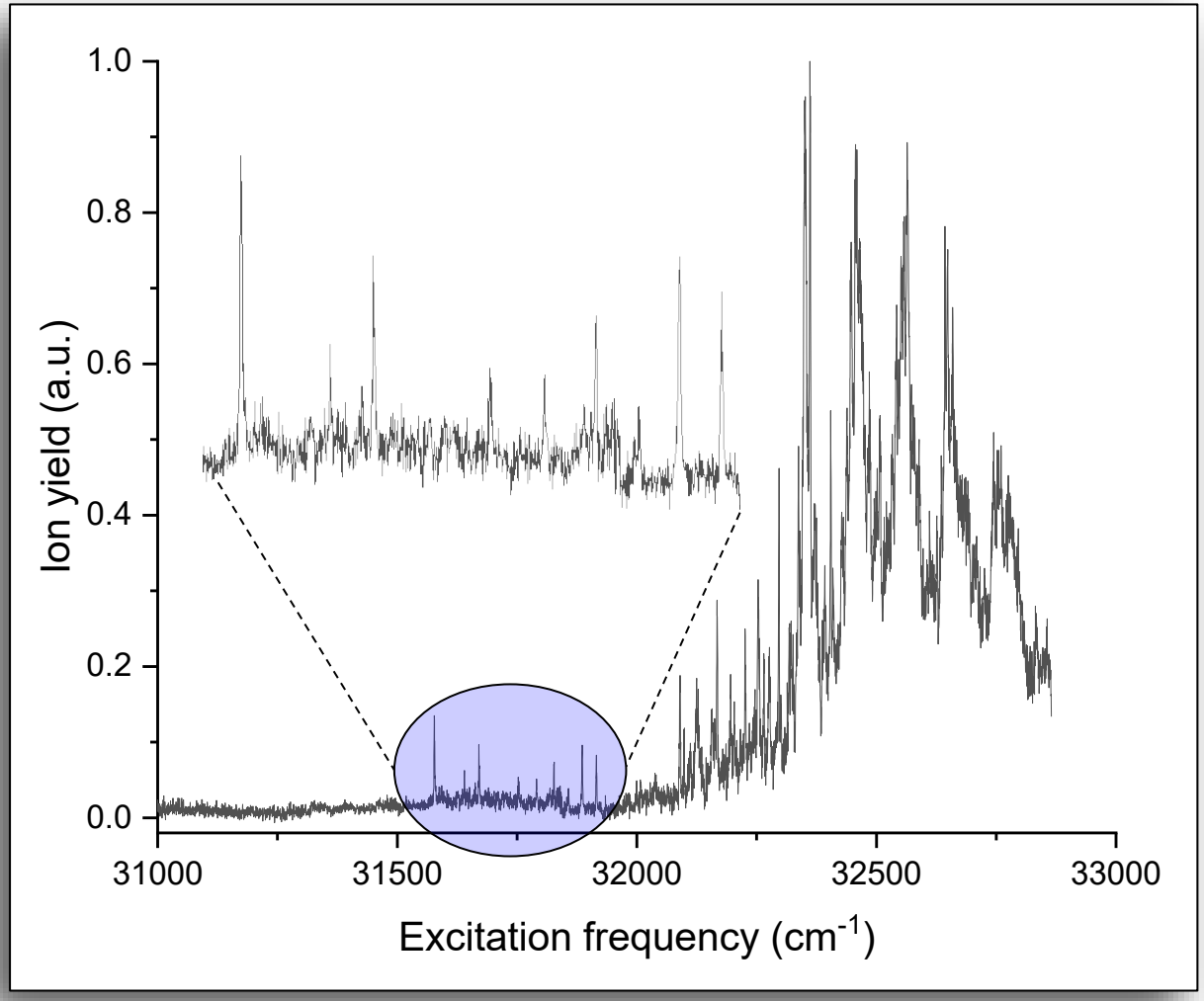



*Benchmark for interpreting UA studies*

W.L. Ryan and D.H. Levy, *J. Am. Chem. Soc.* **2001**, *123, 961*

# Excitation spectroscopy - but without heating

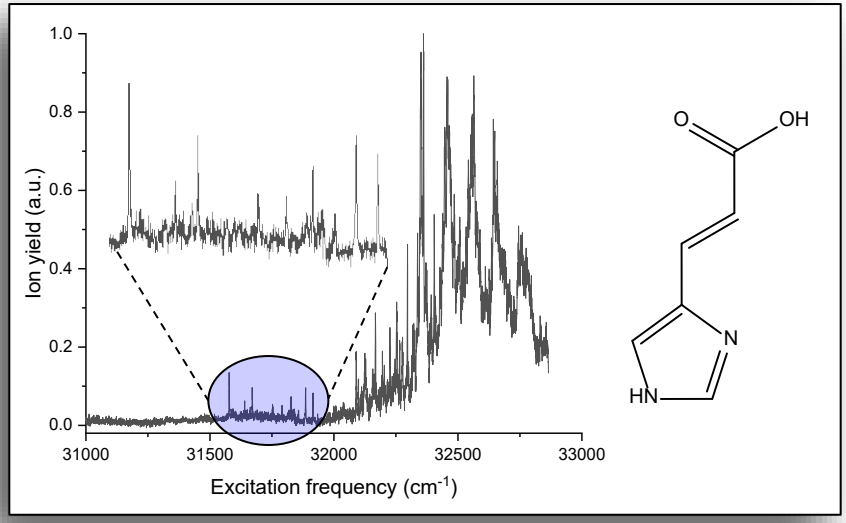


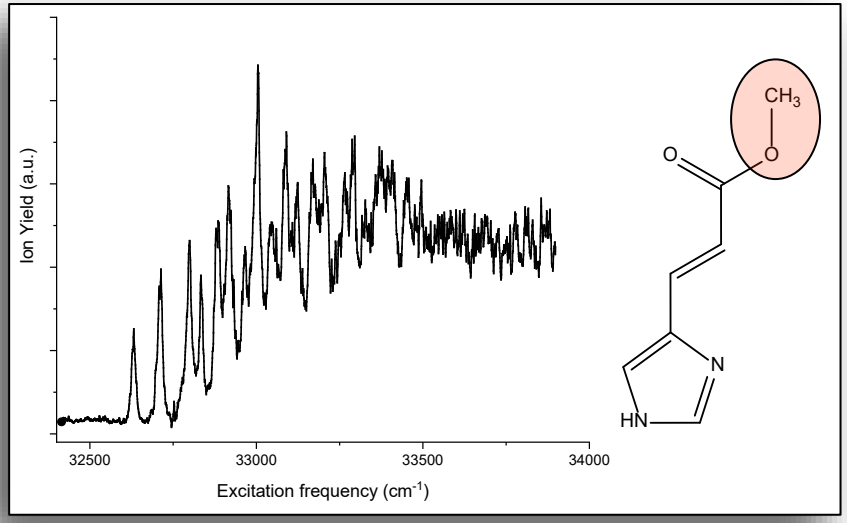

- Degenerate $n\pi^*$ and $\pi\pi^*$ states
- *Long-lived* $n\pi^*$ state
- *Ultrafast* $\pi\pi^* \rightarrow n\pi^*$ internal conversion

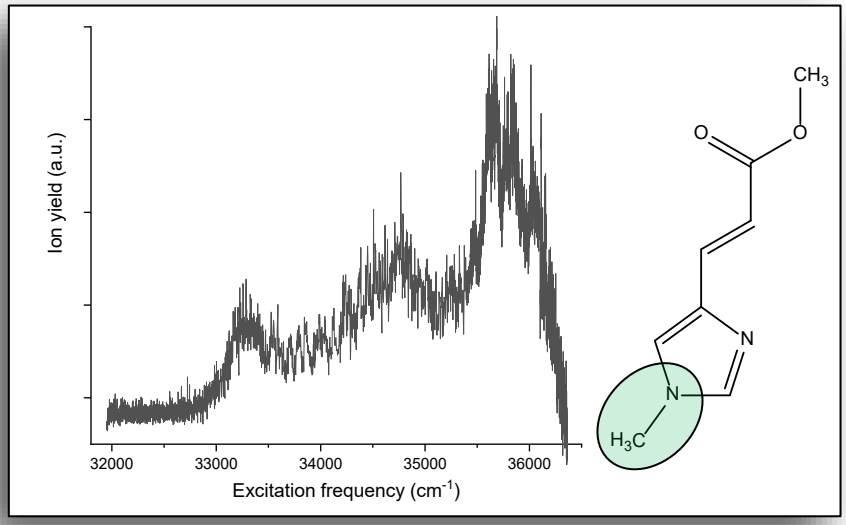
Solvation in polar solvents removes *harmful decay pathways*

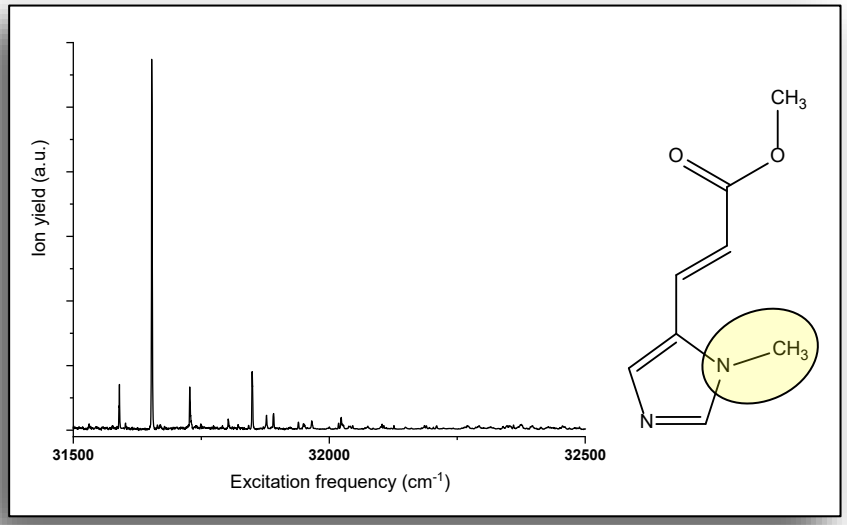
# Tailoring urocanic acid as molecular heater

Mol Phot



# Light on the dark side of the force

*"The dark side clouds everything. Impossible to see the light, the future is"*

but fortunately there is spectroscopy …

# Light on the dark side of the force

# Light on the dark side of the force

# Conclusions

- High-resolution laser spectroscopy essential for modelling astronomical observations and understanding astronomical PAH inventory
  - *(Dominating) role of anharmonicity*
  - *Detailed fingerprints of global structure*
  - *Benchmark for quantum chemical calculations*

- High-resolution laser spectroscopy key to reading manual of light-activated molecular materials and optimizing them
  - *Details potential energy surfaces accessible by resolved vibronic activity*
  - *Elucidation of photoreactive pathways*
  - *Microsolvation enables controlling interactions with environment*

# Conclusions

- High-resolution laser spectroscopy offers key insight into pathways that convert photon energy into heat
  - *Dependence potential energy surfaces of electronically excited states on detailed spatial structure and solvent environment*
  - *Elucidating harmful decay pathways (and how to avoid them)*
  - *Exploration 'novel' chromophore motifs as employed by nature*

# Funding

Mol Phot

INNOVATION EXCHANGE AMSTERDAM IXA Physics2Market

NWO
Nederlandse Organisatie voor Wetenschappelijk Onderzoek

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

Leopoldina
Nationale Akademie der Wissenschaften

FOM

BOOST CROP

SEVENTH FRAMEWORK PROGRAMME

EC-TMR (RTN), EC-FET,
EC-NMP, EC-Marie Curie

# *May the photons be with you …*

Mol Phot