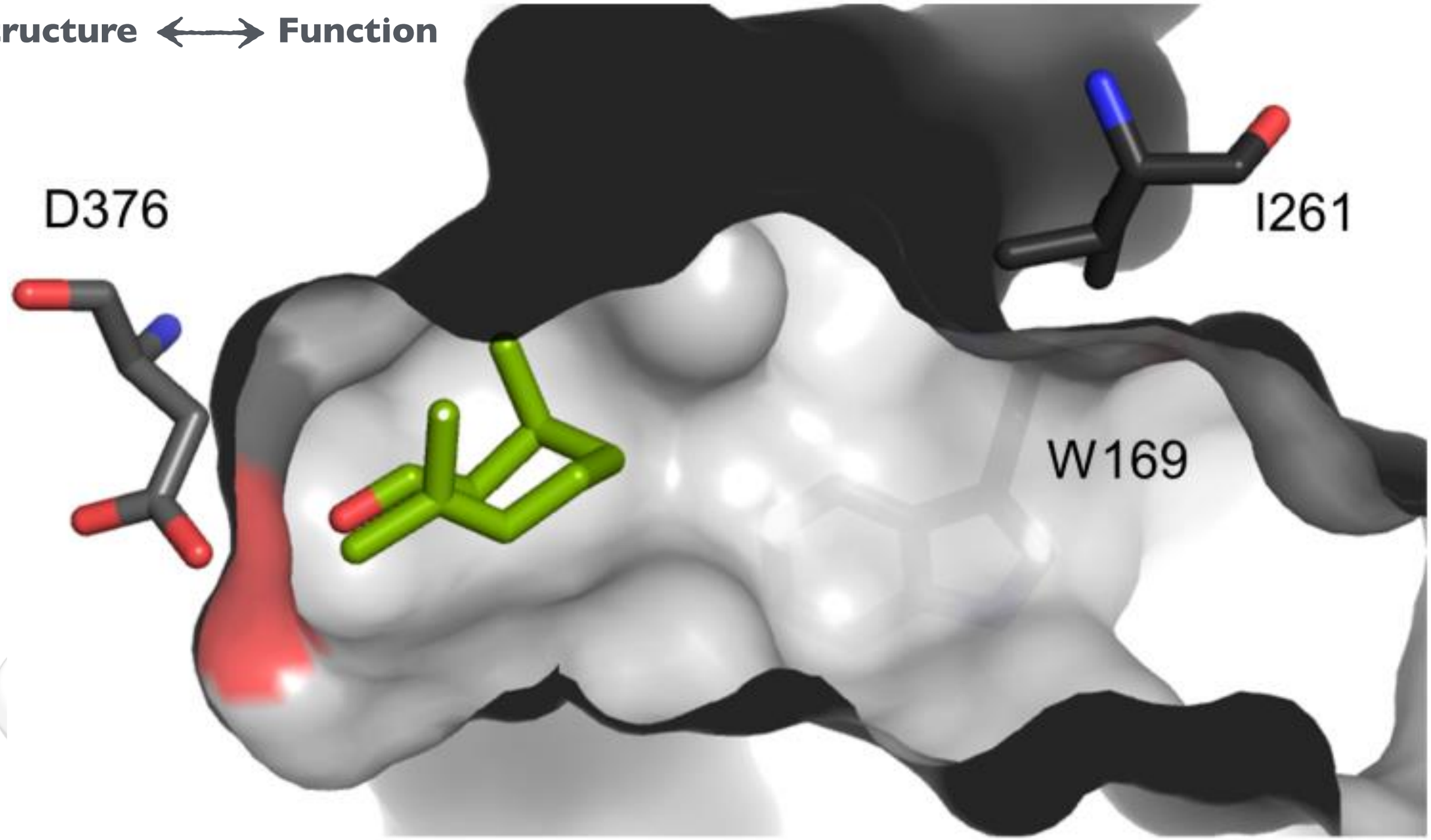
Molecular structure elucidation and beyond with microwave rotational spectroscopy

Sérgio R. Domingos | **Center for Physics of the University of Coimbra** | **Portugal**

CFisUC

1 2 9 0 UNIVERSIDADE D COIMBRA

Structure ⟷ Function



Hammer S. C. et al. *Nat. Chem. Biol.* (**2015**) 11, 121-126
Stary A. et al. *Biochem. Biophys. Res. Commun.* (**2007**) 361, 941-945

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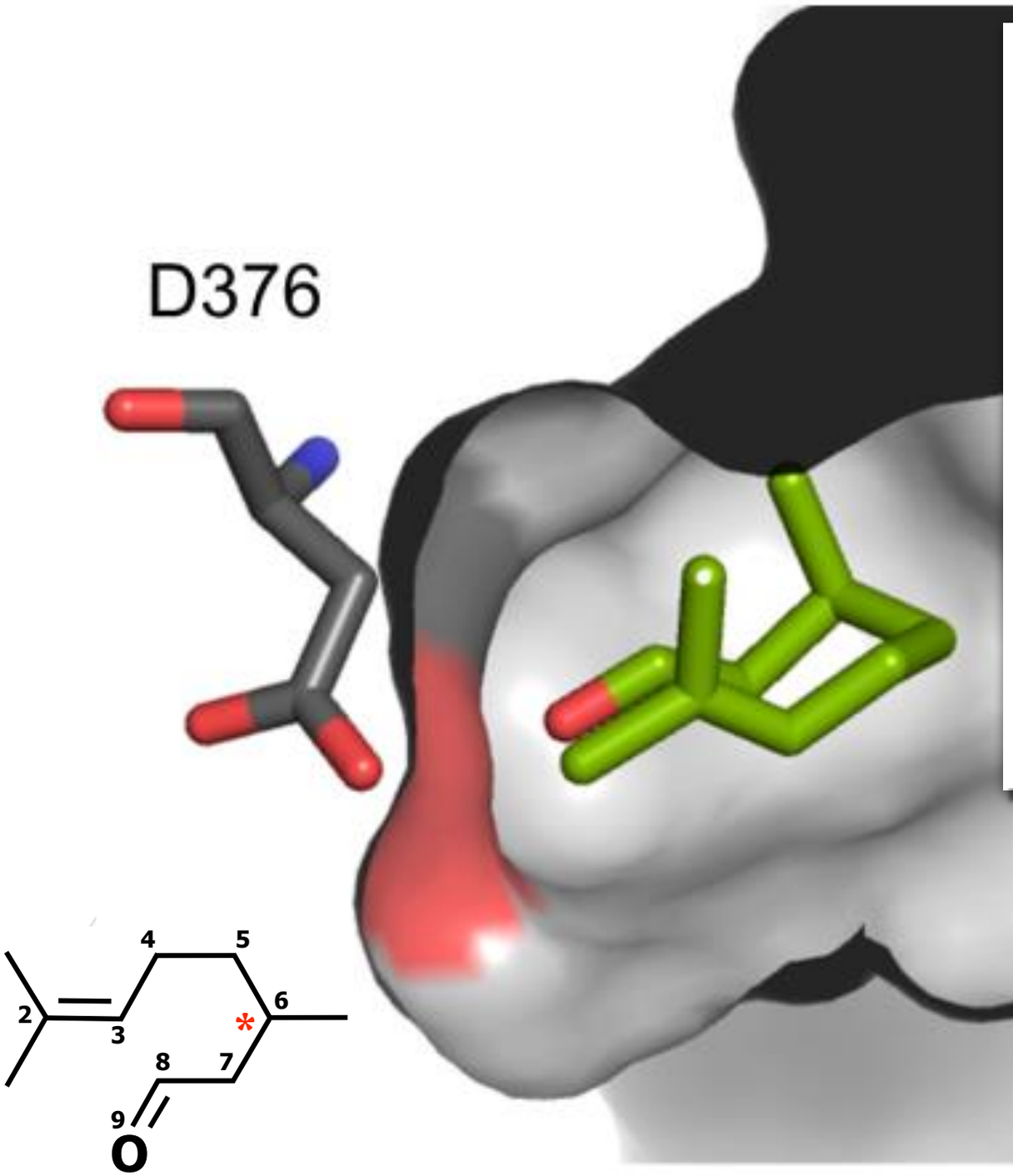

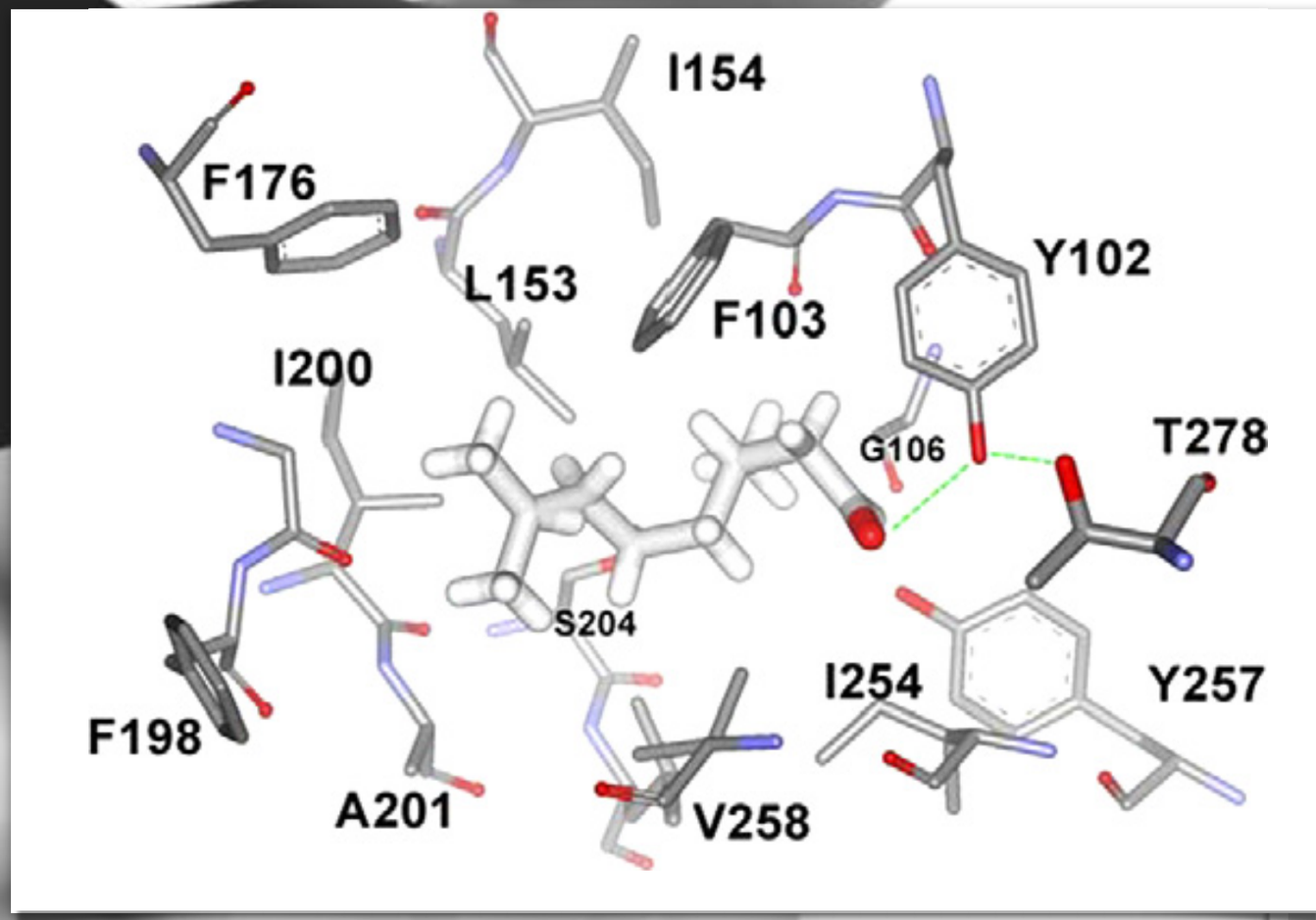

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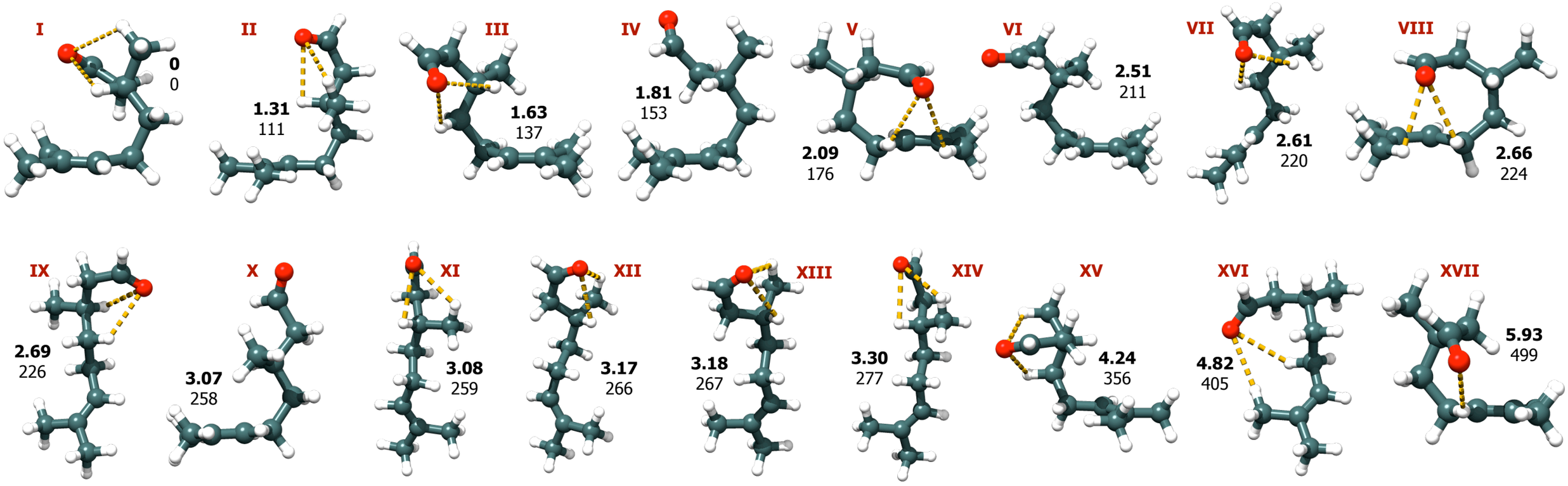
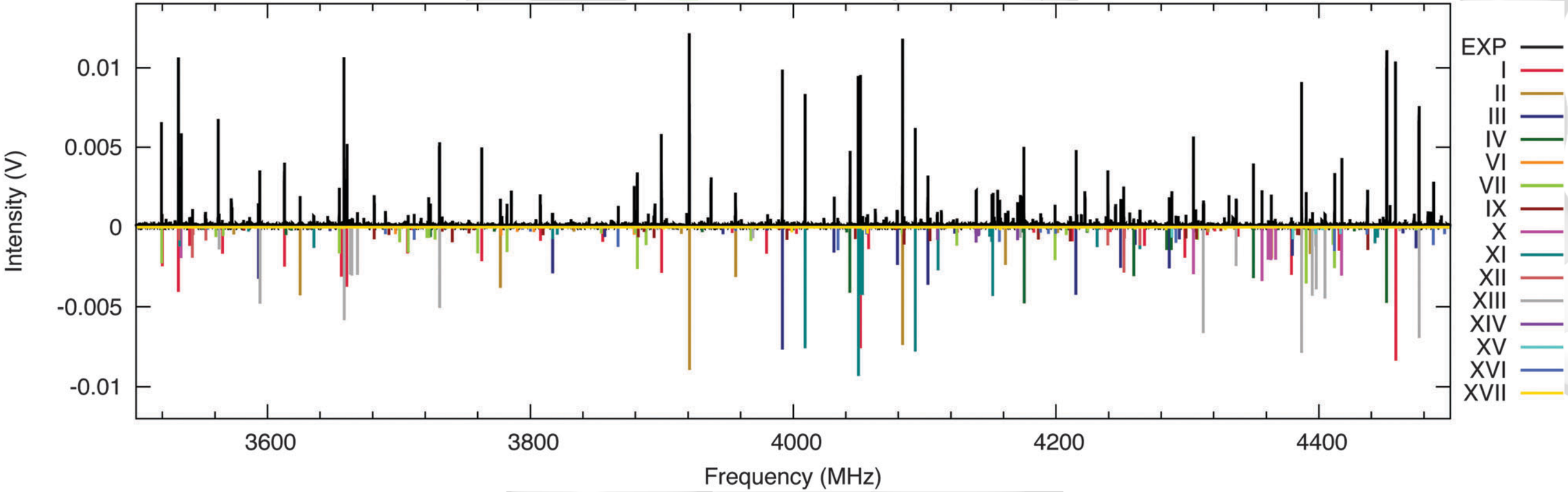
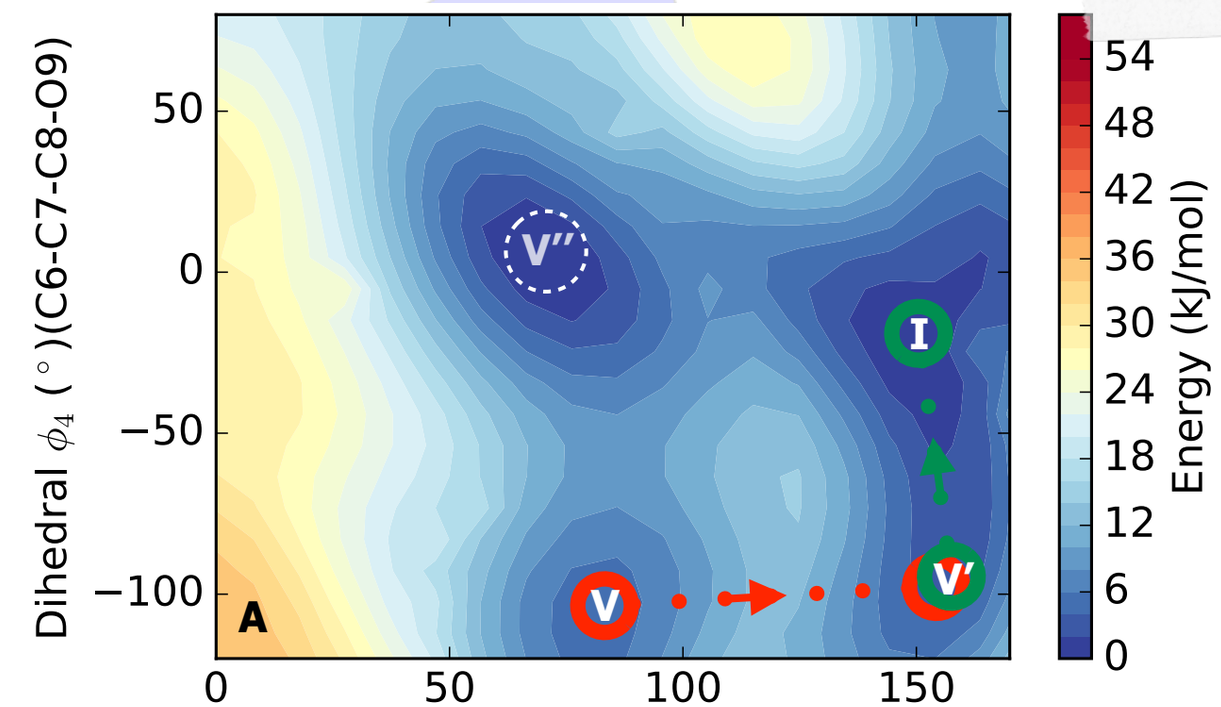
Stary A. et al. *Biochem. Biophys. Res. Commun.* (**2007**) 361, 941-945

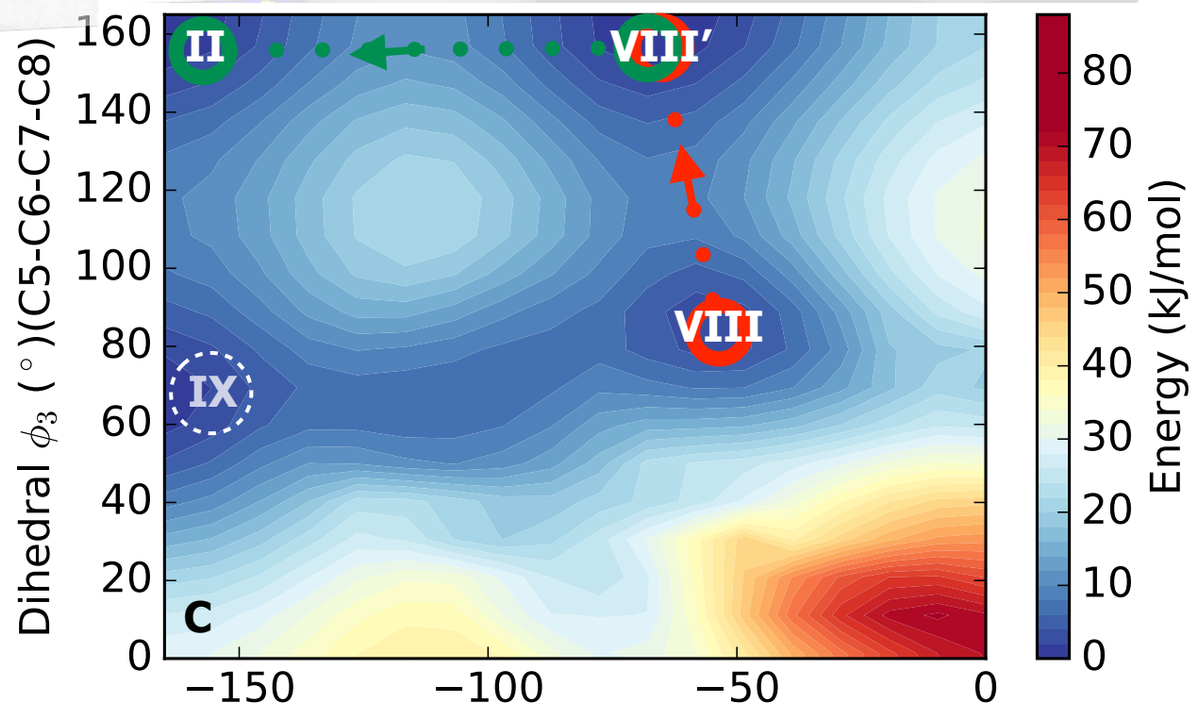


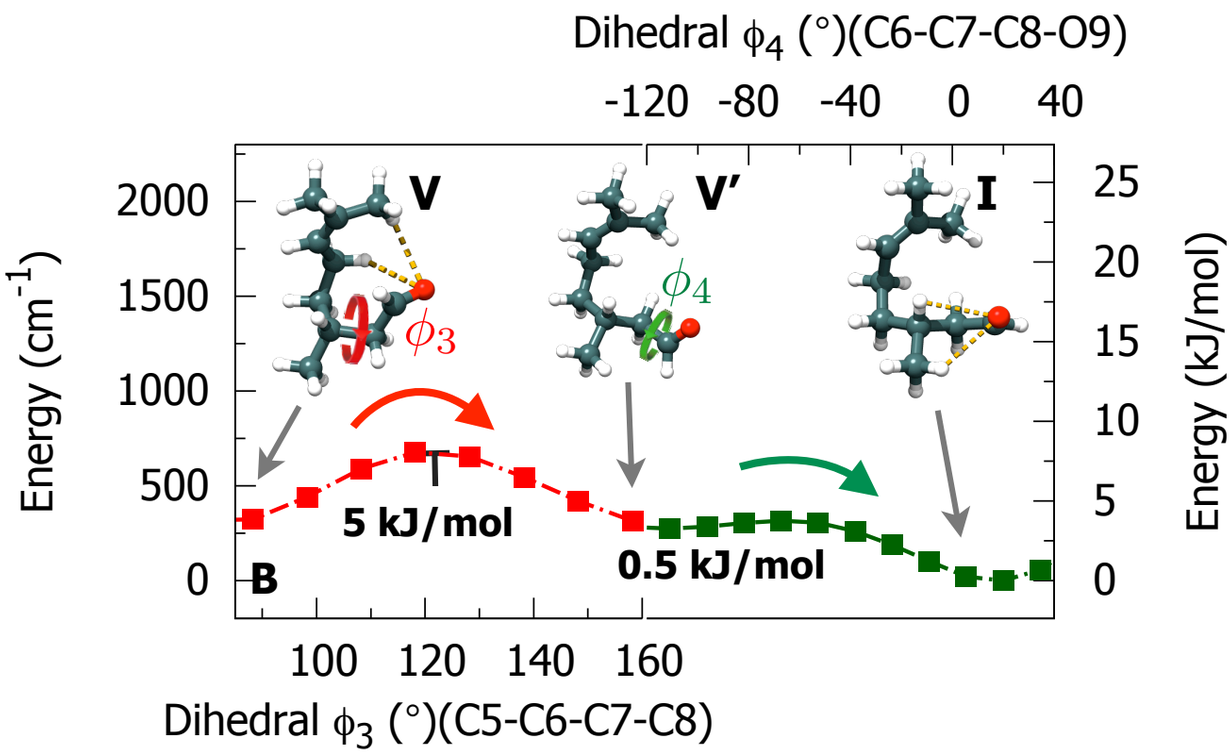


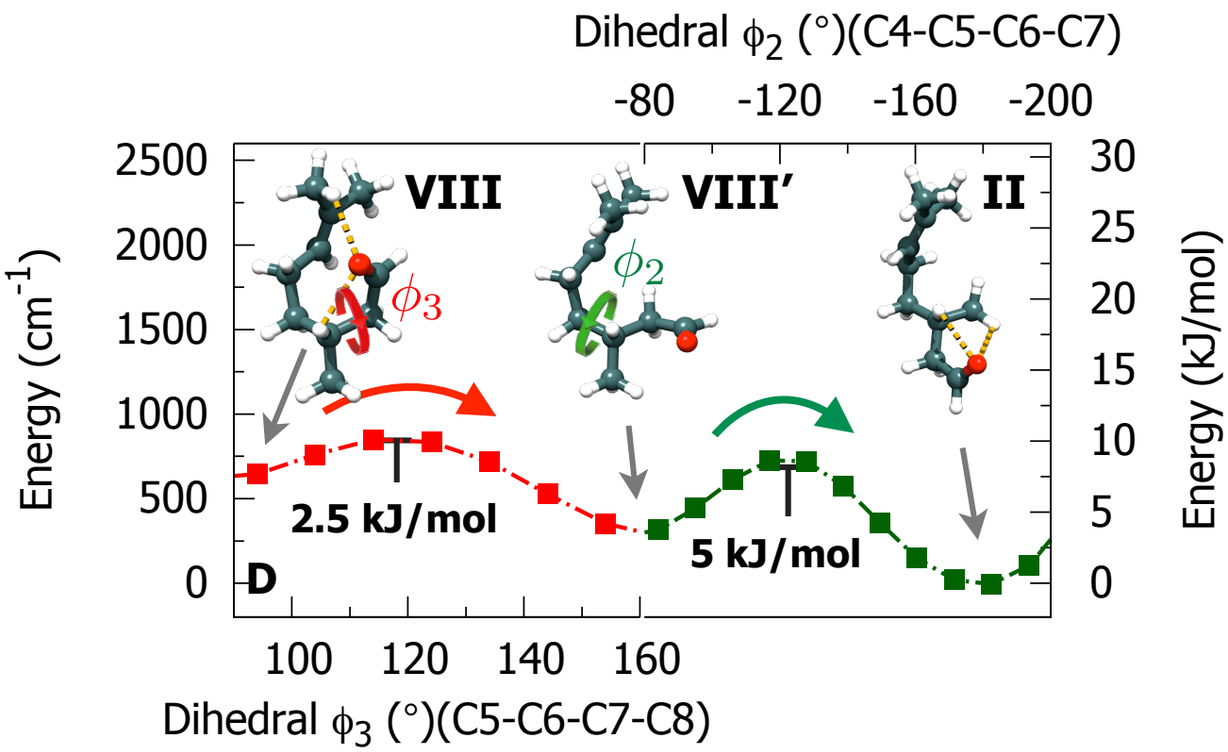
Spectrum ⟷ Structure

Phys. Chem. Chem. Phys. (**2016**) 18, 16682-16689



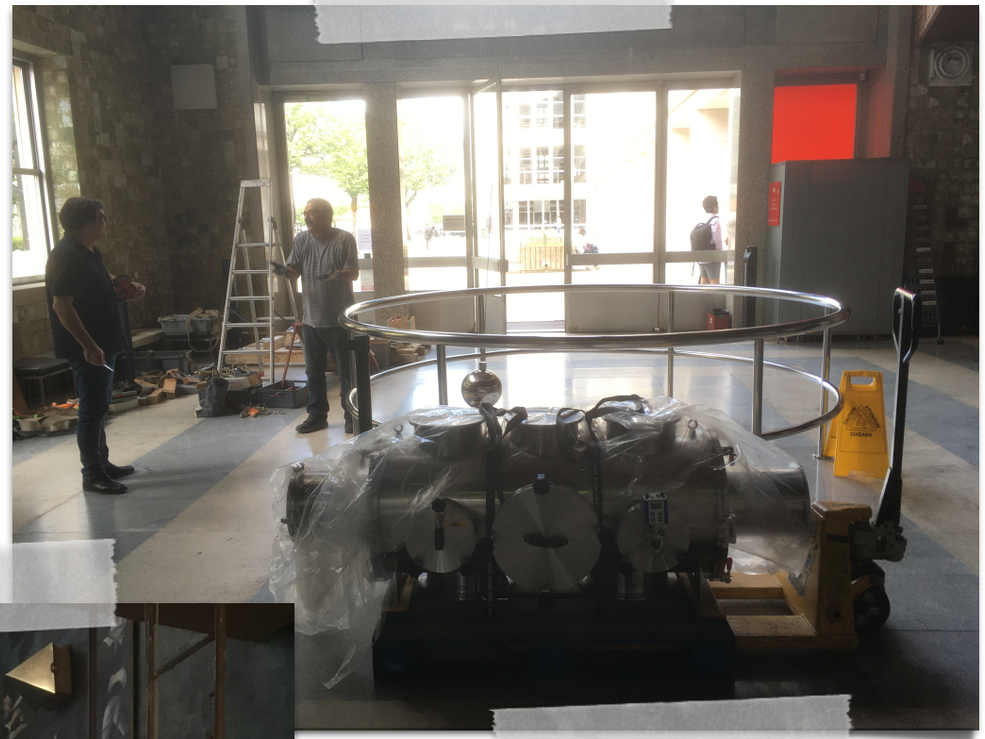






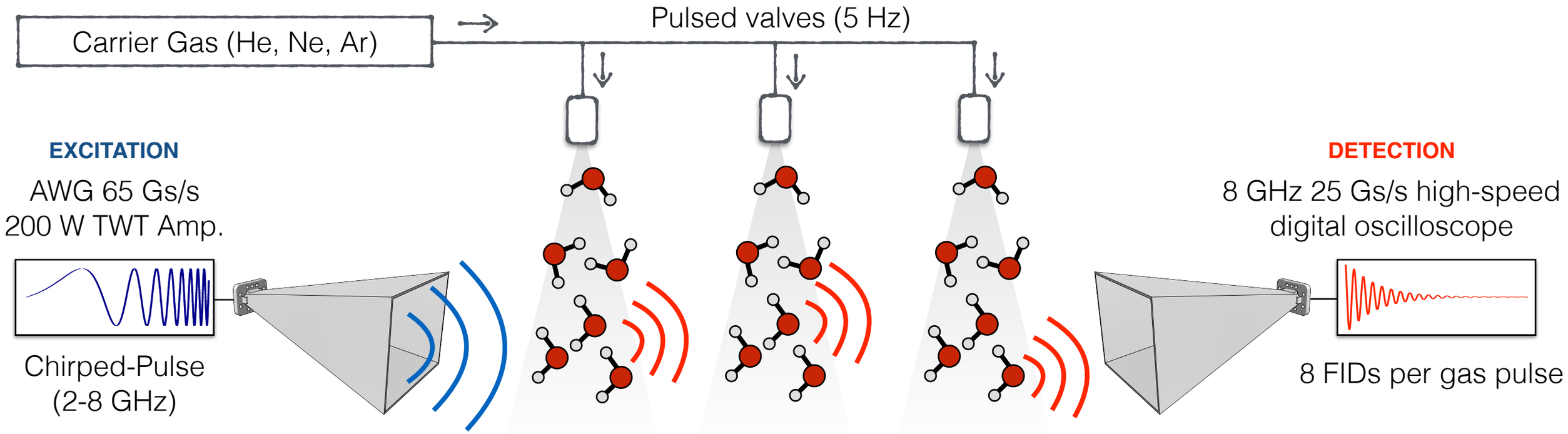
Phys. Chem. Chem. Phys. (**2016**) 18, 16682-16689

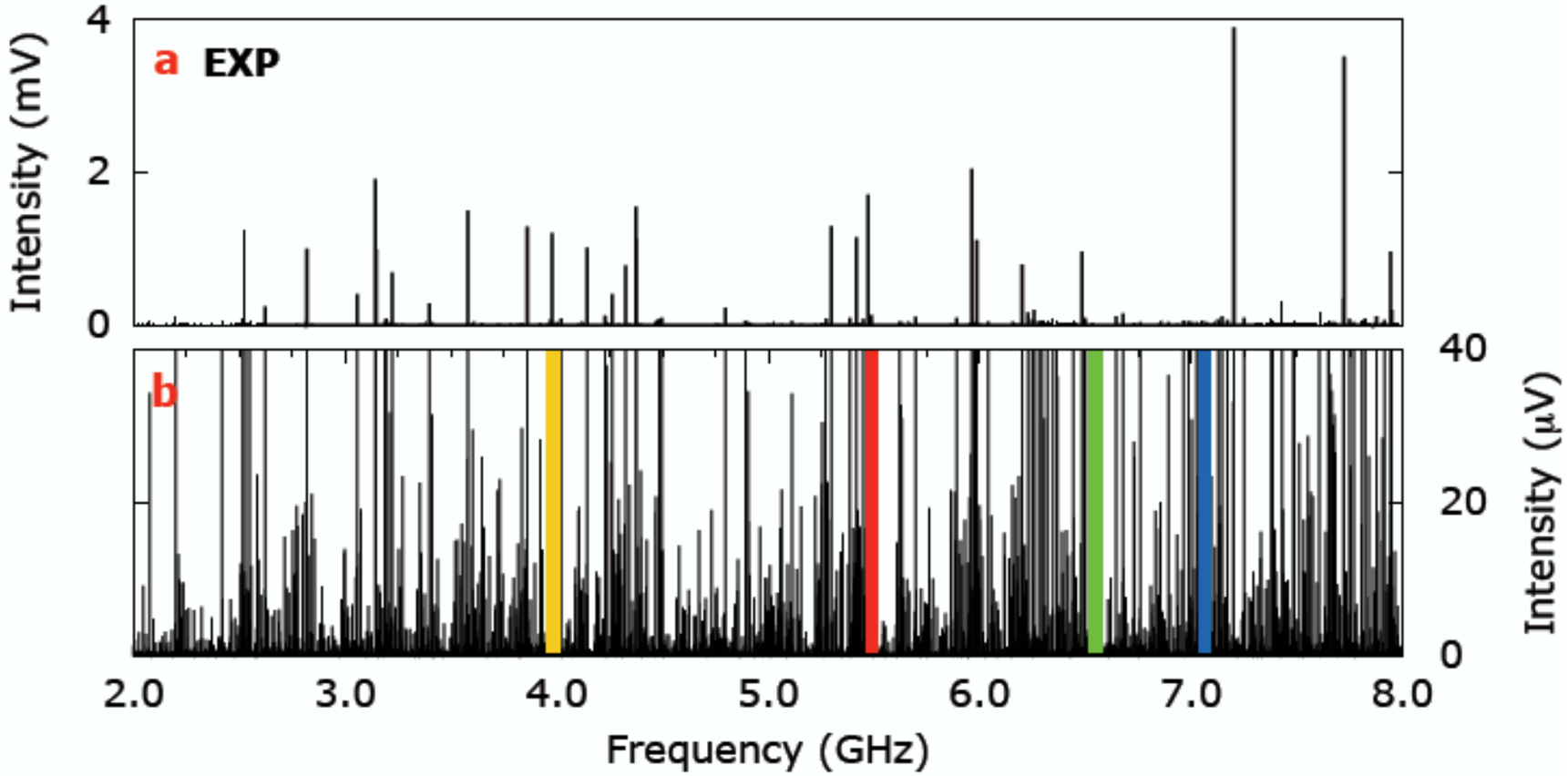

CAUTION
ATTENTION
CUIDADO




OEXTER

Multi-nozzle chirped-pulse FT microwave spectrometer



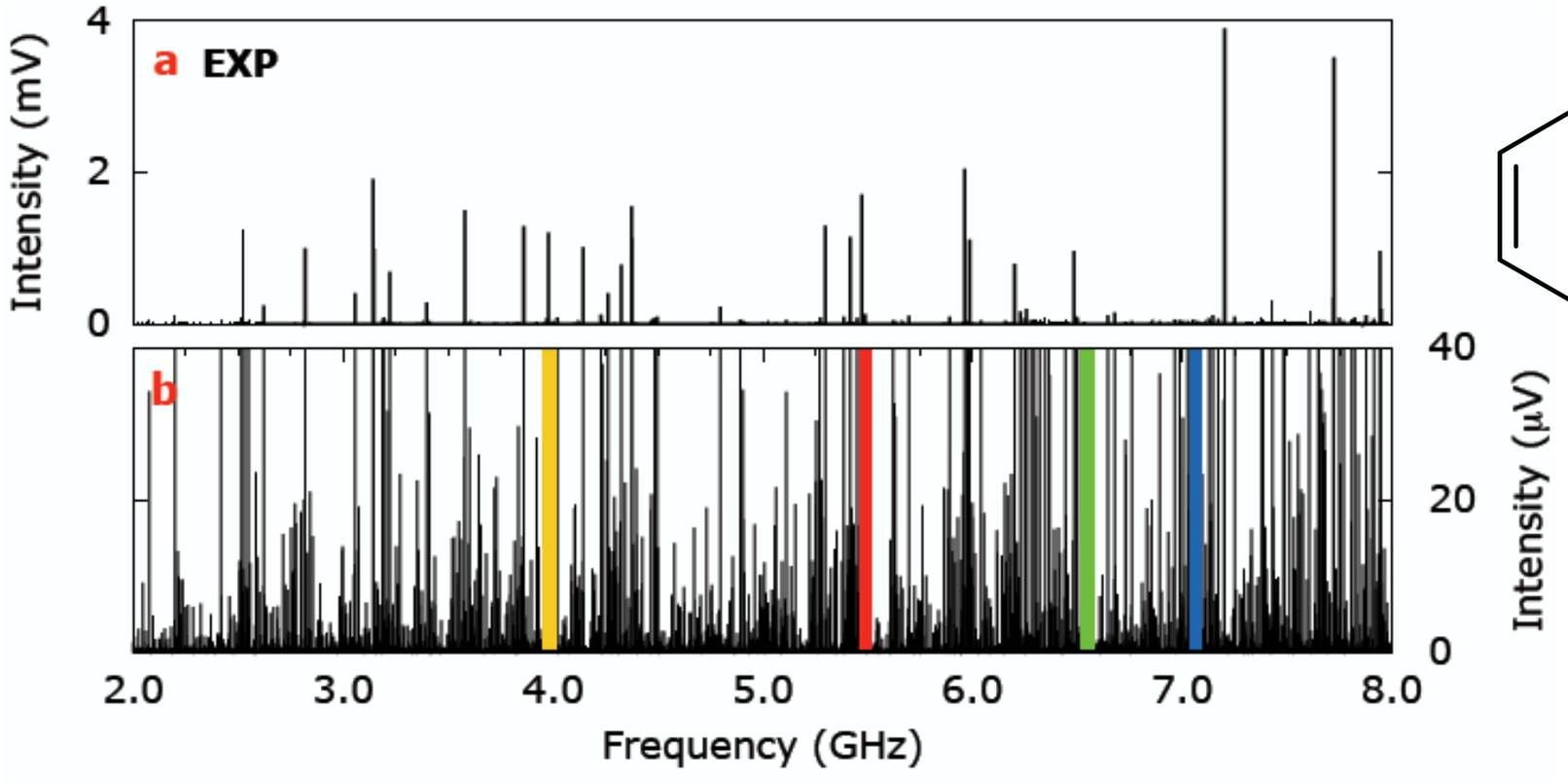


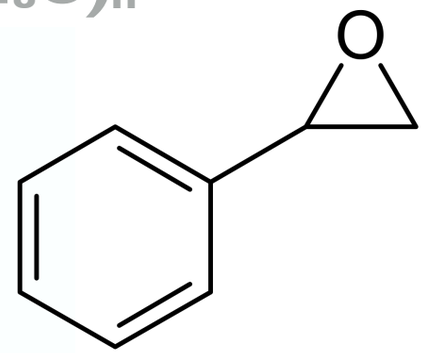
Specs:

6 GHz
single shot bandwidth
10^6
resolution elements
25 kHz
frequency accuracy
40 Hz
effective rep rate
~1M avg FIDs
in 12h measurement time

Commun. Chem. 4 (32) (**2021**)

Rotational spectroscopy of chiral clusters of styrene oxide $(C_8H_8O)_n$





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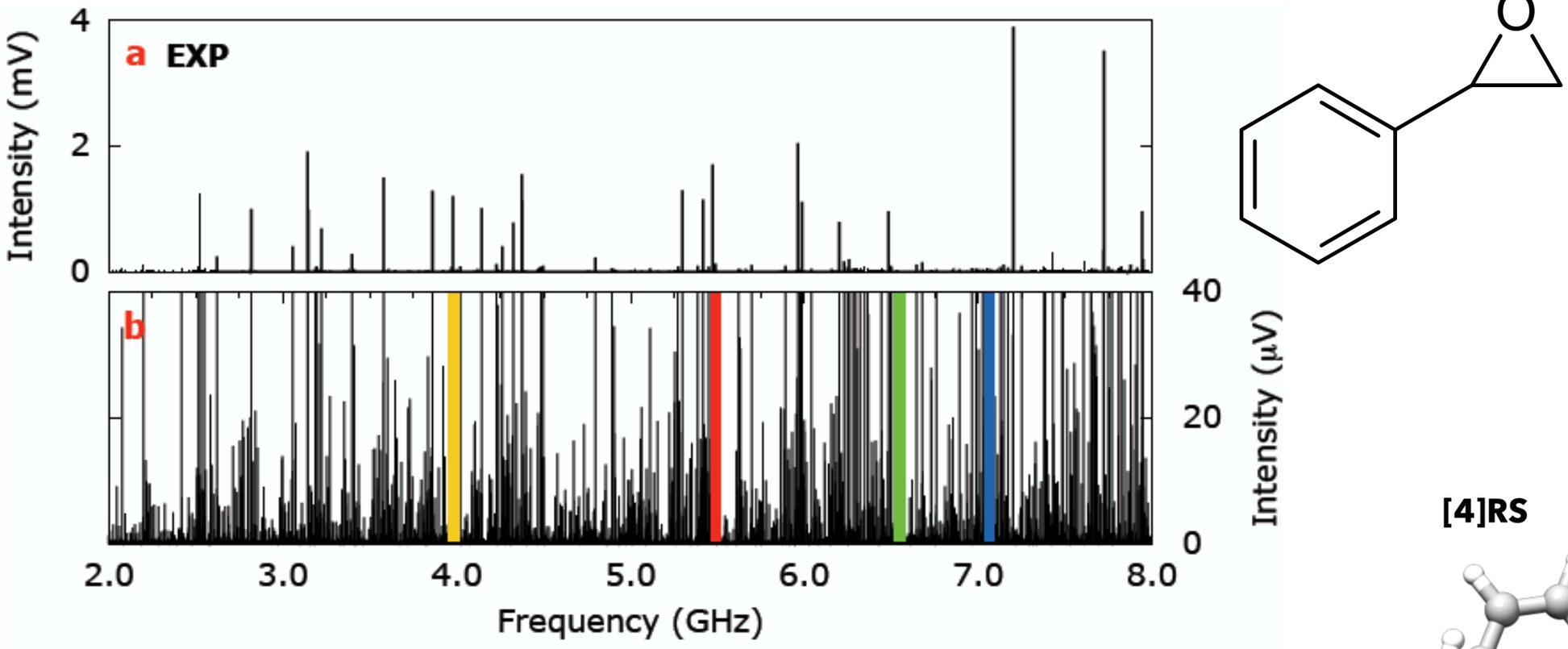
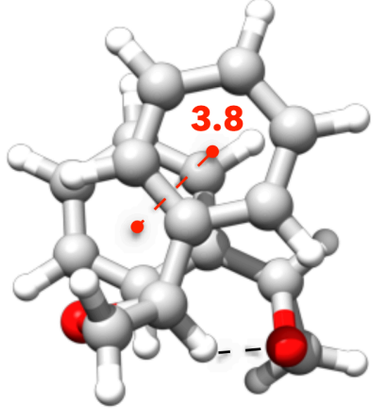
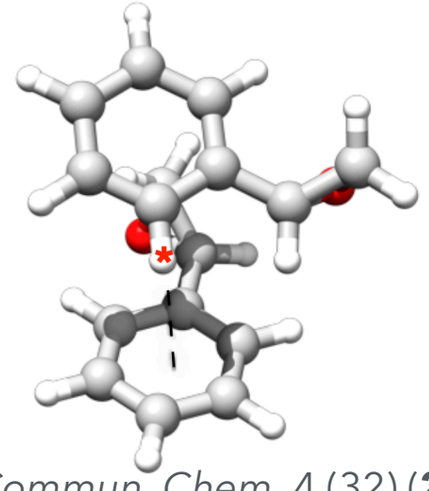
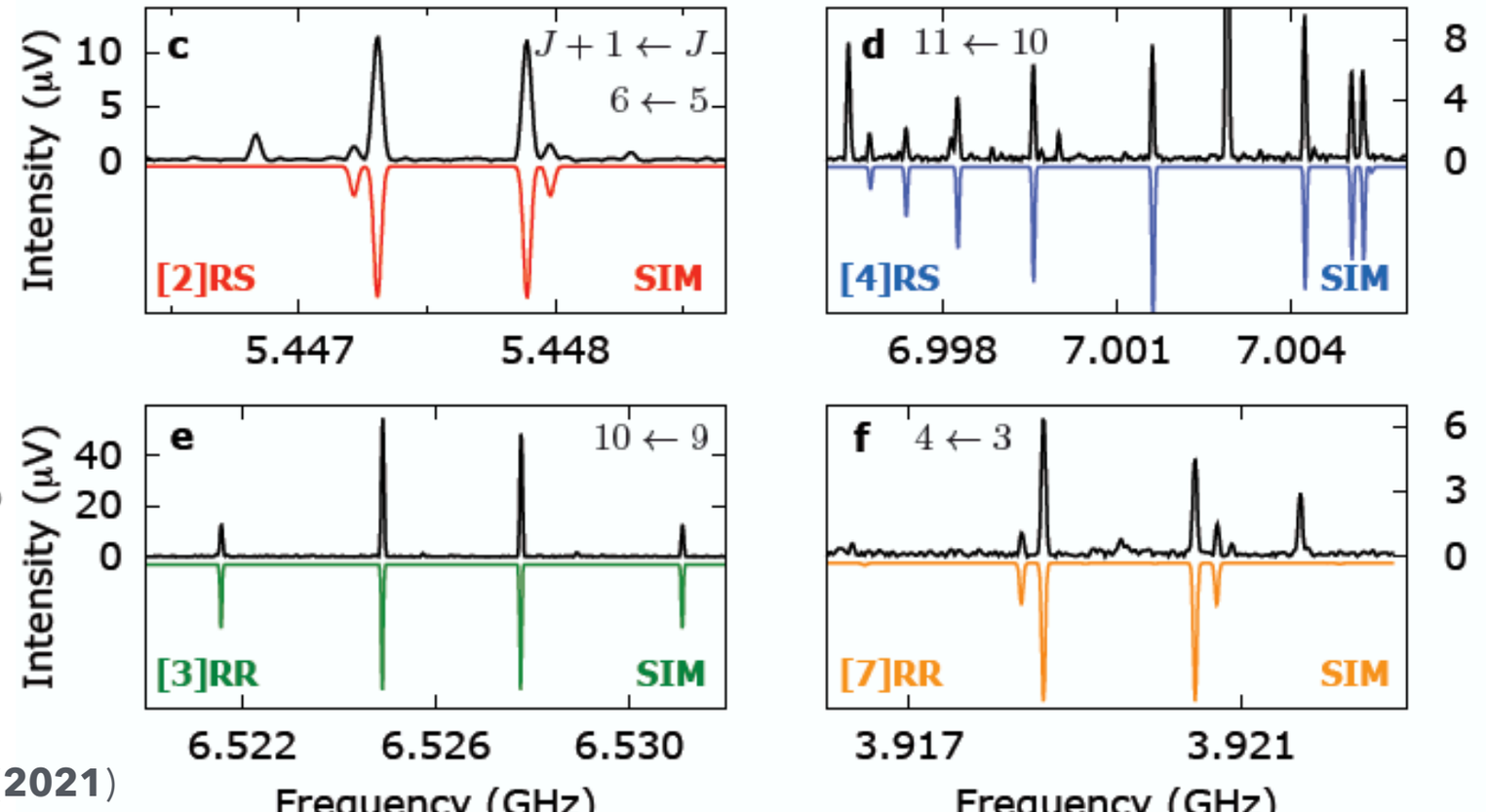


[2]RS

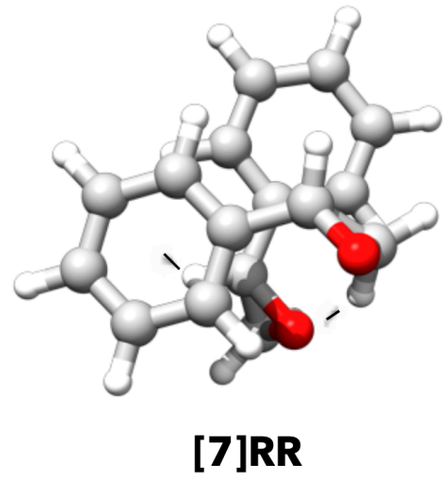


[3]RR

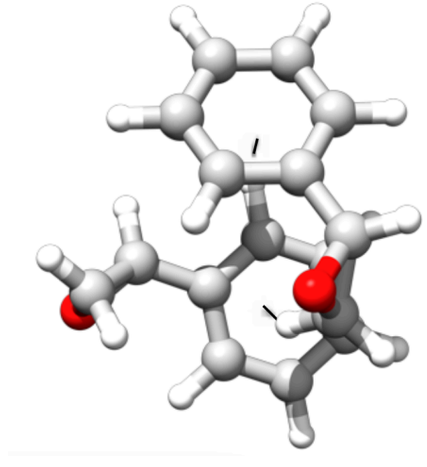




[4]RS



[7]RR



Commun. Chem. 4 (32) (**2021**)

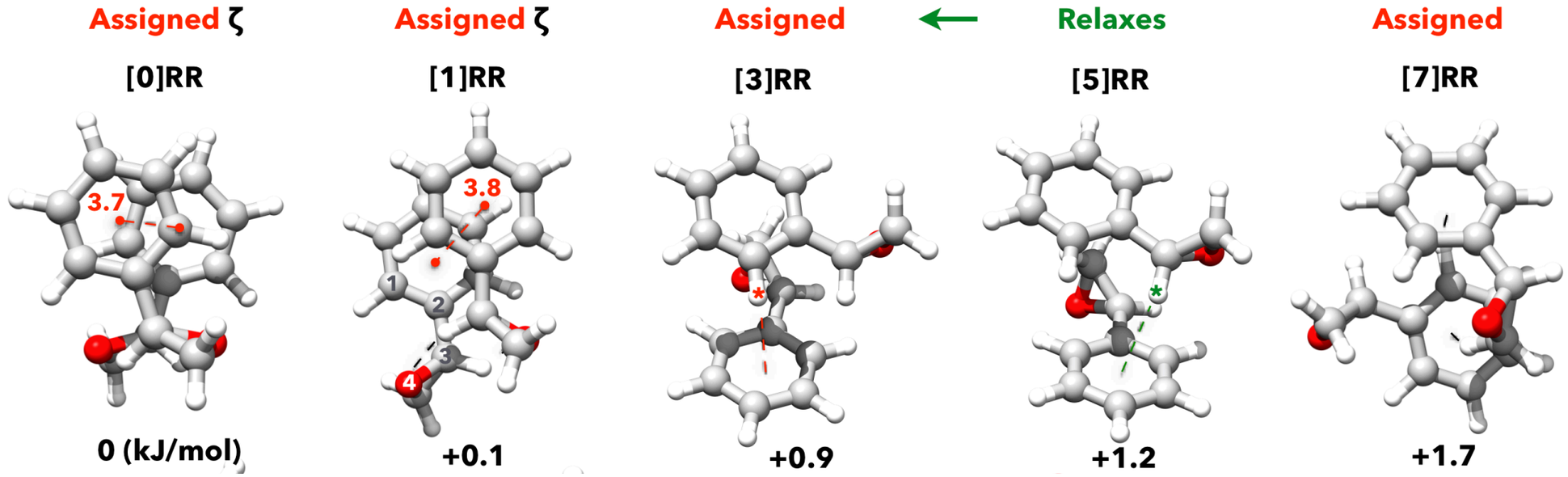
ARTICLE

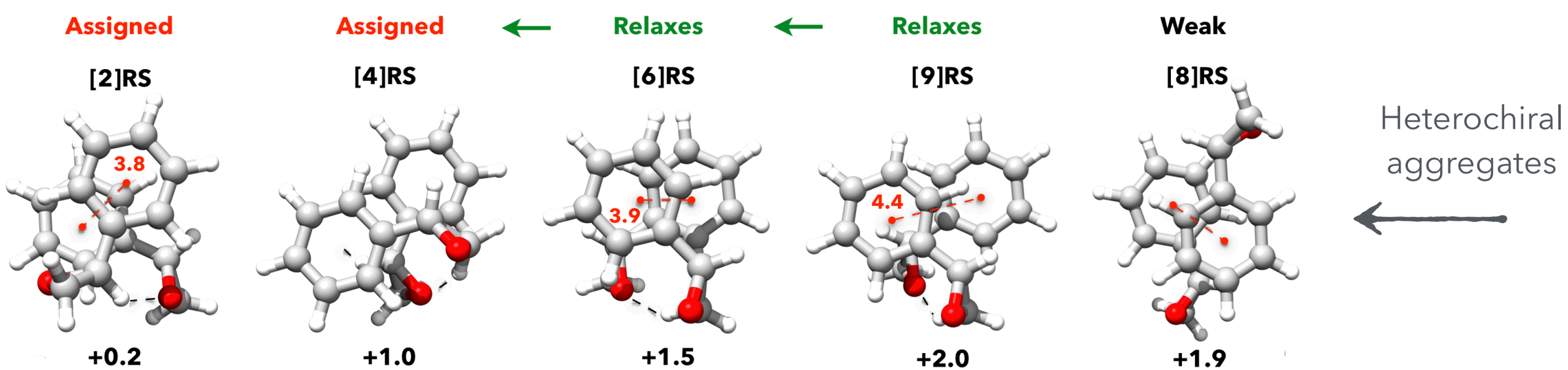
https://doi.org/10.1038/s42004-021-00468-4 OPEN

Check for updates

Dynamic chiral self-recognition in aromatic dimers of styrene oxide revealed by rotational spectroscopy

Homochiral aggregates





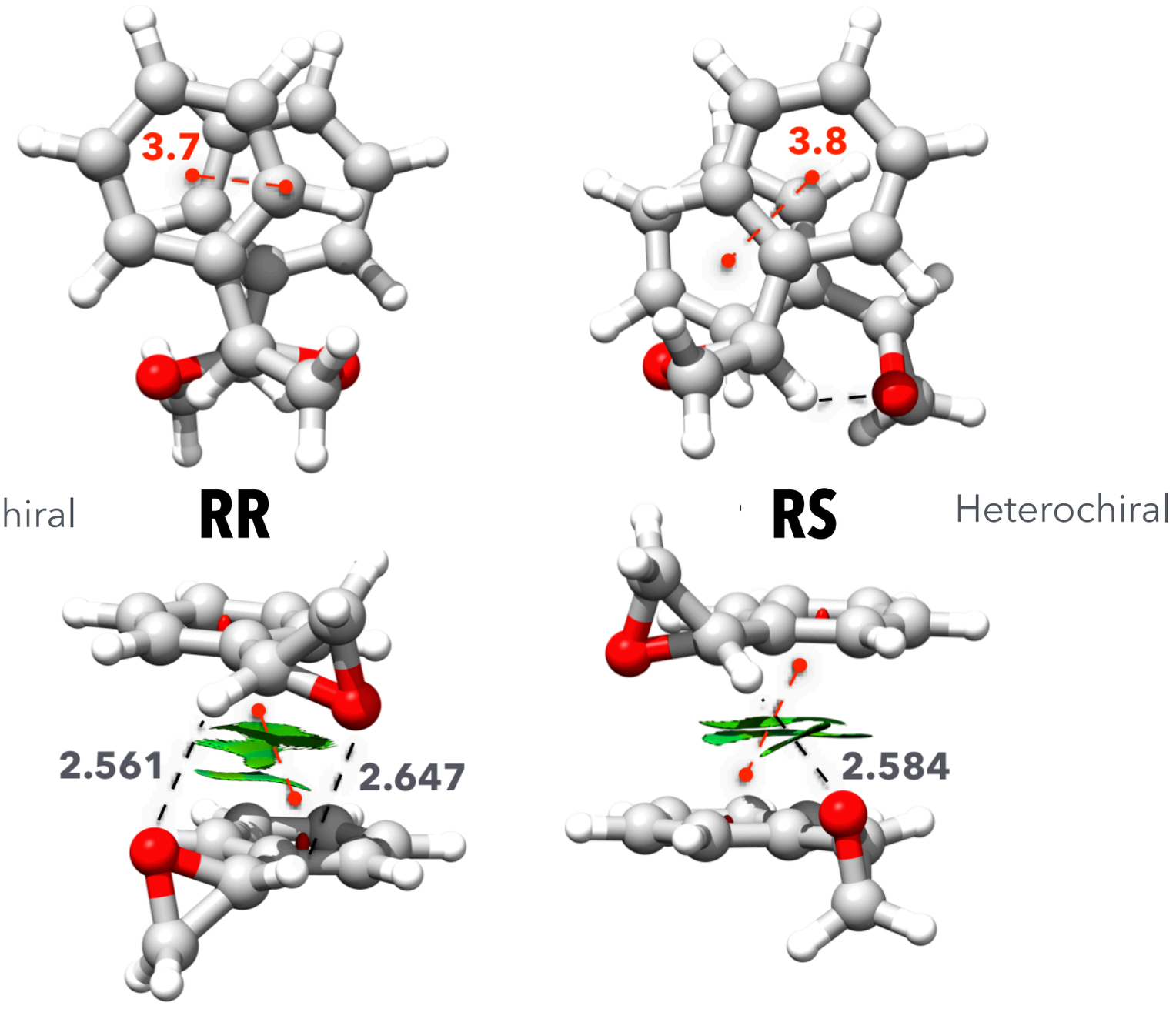
Heterochiral aggregates

ARTICLE

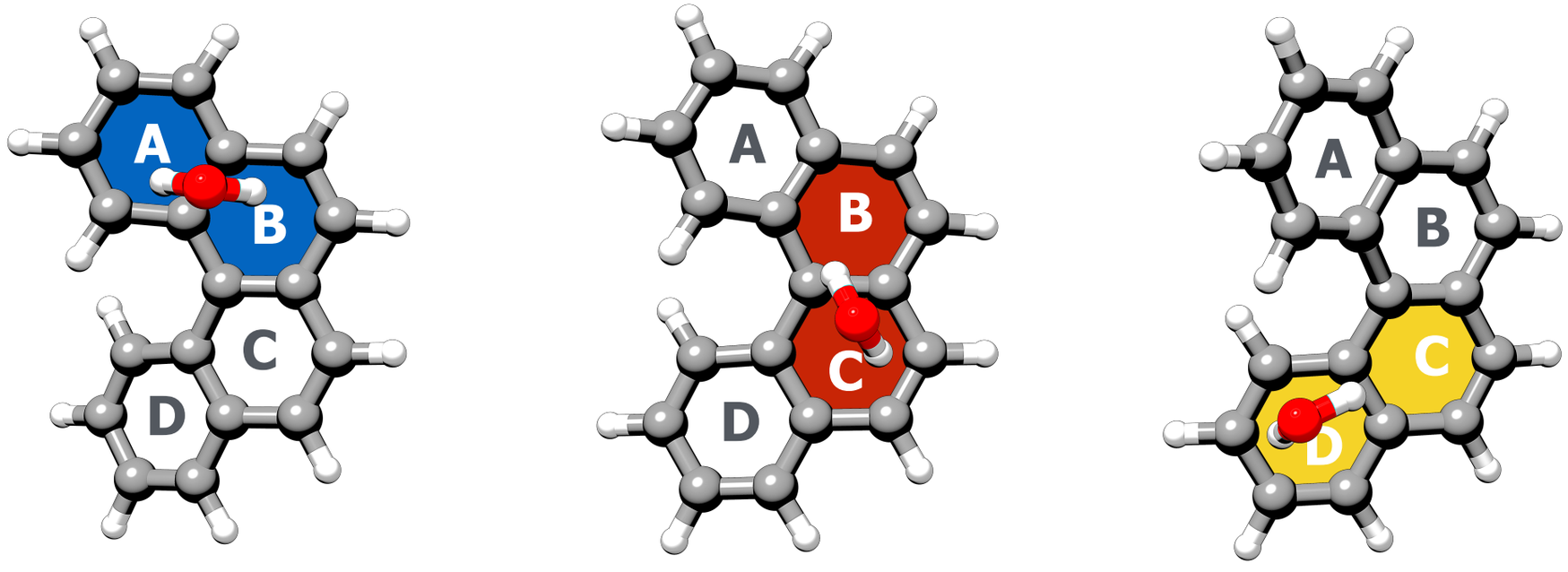
https://doi.org/10.1038/s42004-021-00468-4 OPEN

Check for updates

Dynamic chiral self-recognition in aromatic dimers of styrene oxide revealed by rotational spectroscopy

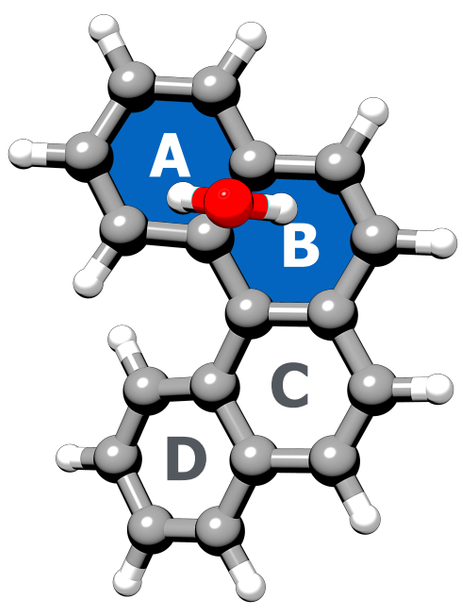


Helical chirality: where is the docking site?

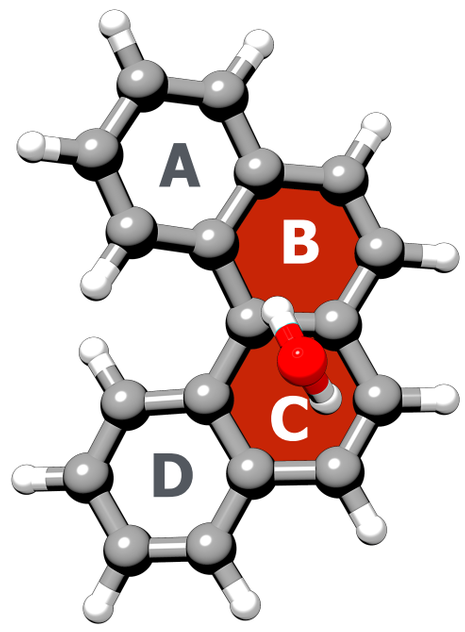


"Water docking bias in [4]helicene" ***Angew. Chem. Int. Ed.*** 58, 1-7. (2019)

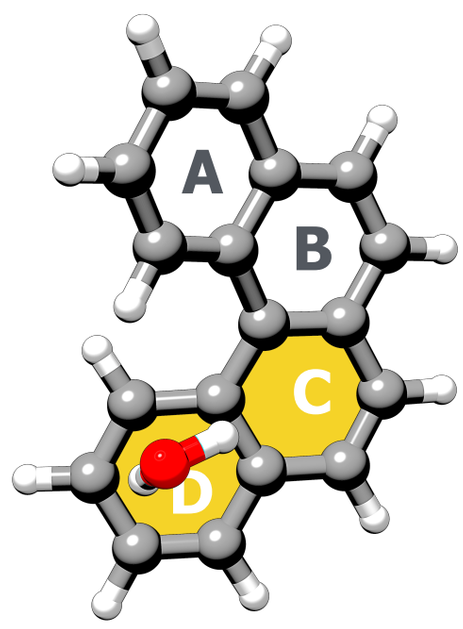
Helical chirality: where is the docking site?



ΔE=+0.45 kJ/mol



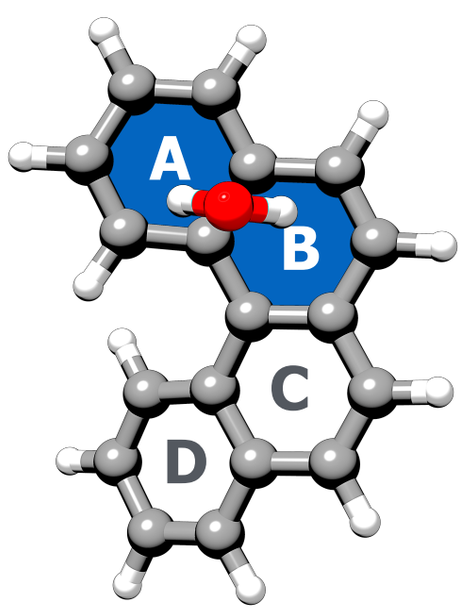
ΔE=+0.56 kJ/mol



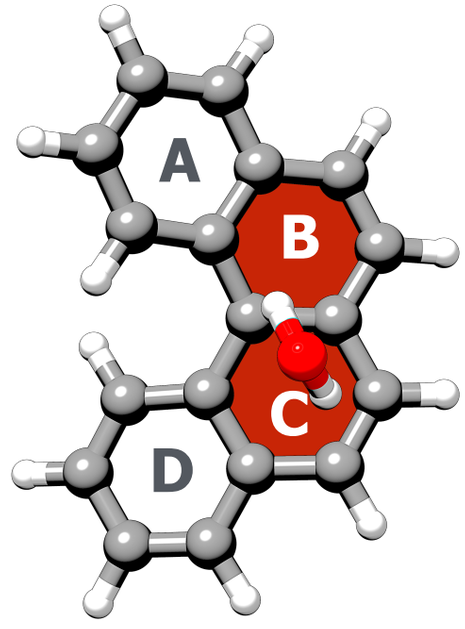
ΔE=0

"Water docking bias in [4]helicene" ***Angew. Chem. Int. Ed.*** 58, 1-7. (2019)

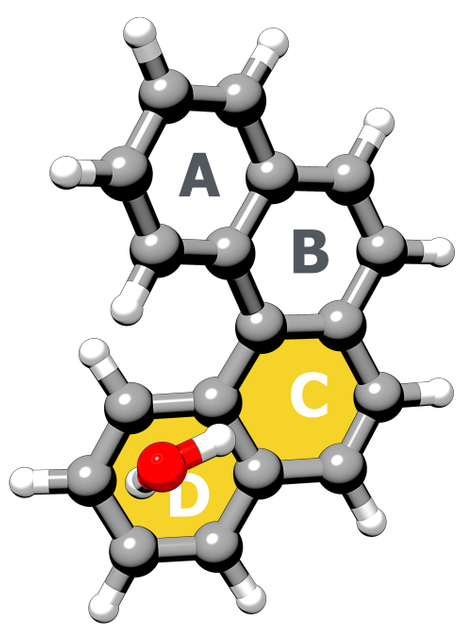
Helical chirality: where is the docking site?



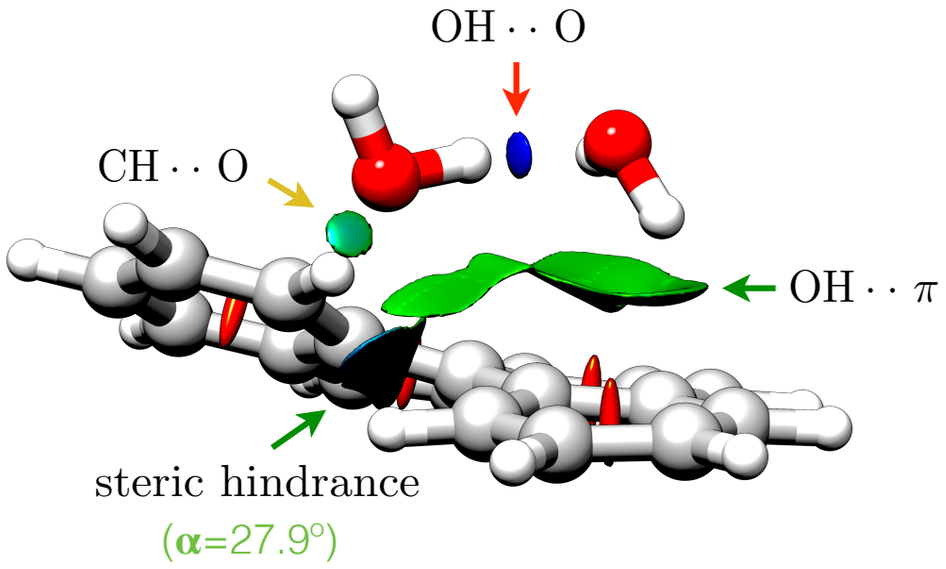
ΔE=+0.45 kJ/mol

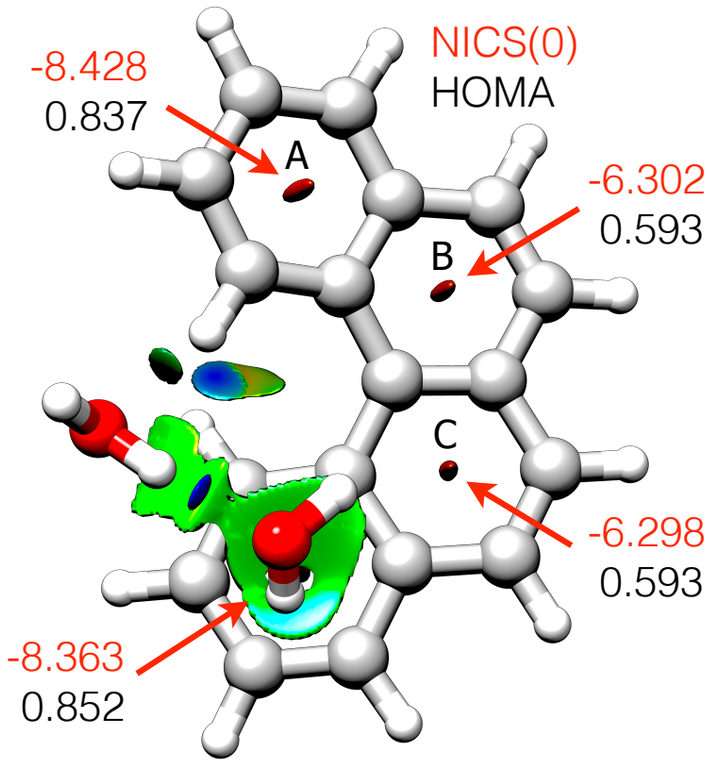


ΔE=+0.56 kJ/mol



ΔE=0



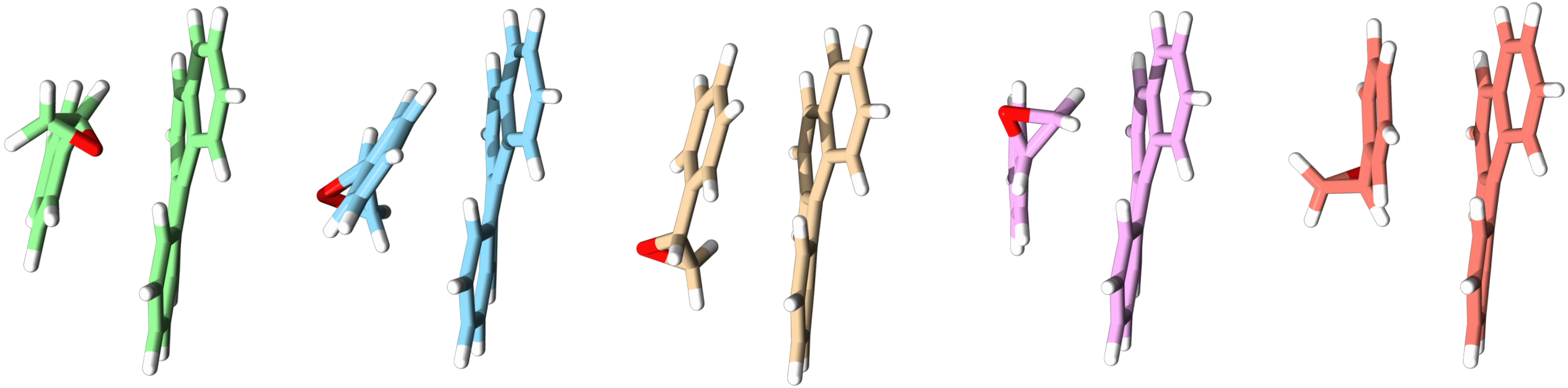


"Water docking bias in [4]helicene" ***Angew. Chem. Int. Ed.*** 58, 1-7. (2019)

Helical chirality: where is the docking site.. **If the ligand is aromatic?**

Helical chirality: where is the docking site.. **If the ligand is aromatic?**

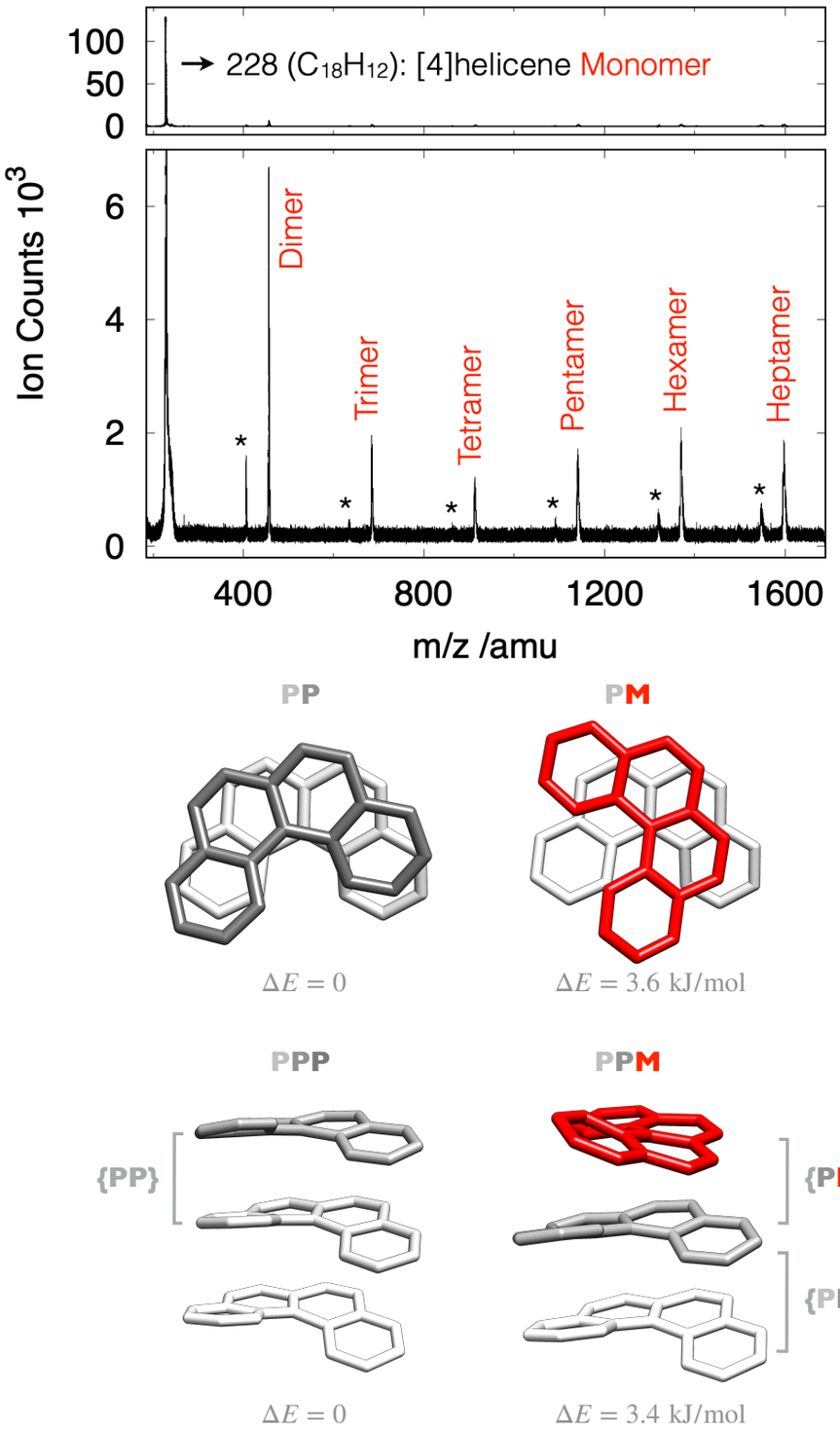
Predicted complexation pairs at the B3LYP-D3BJ/aug-cc-pVTZ level of theory.

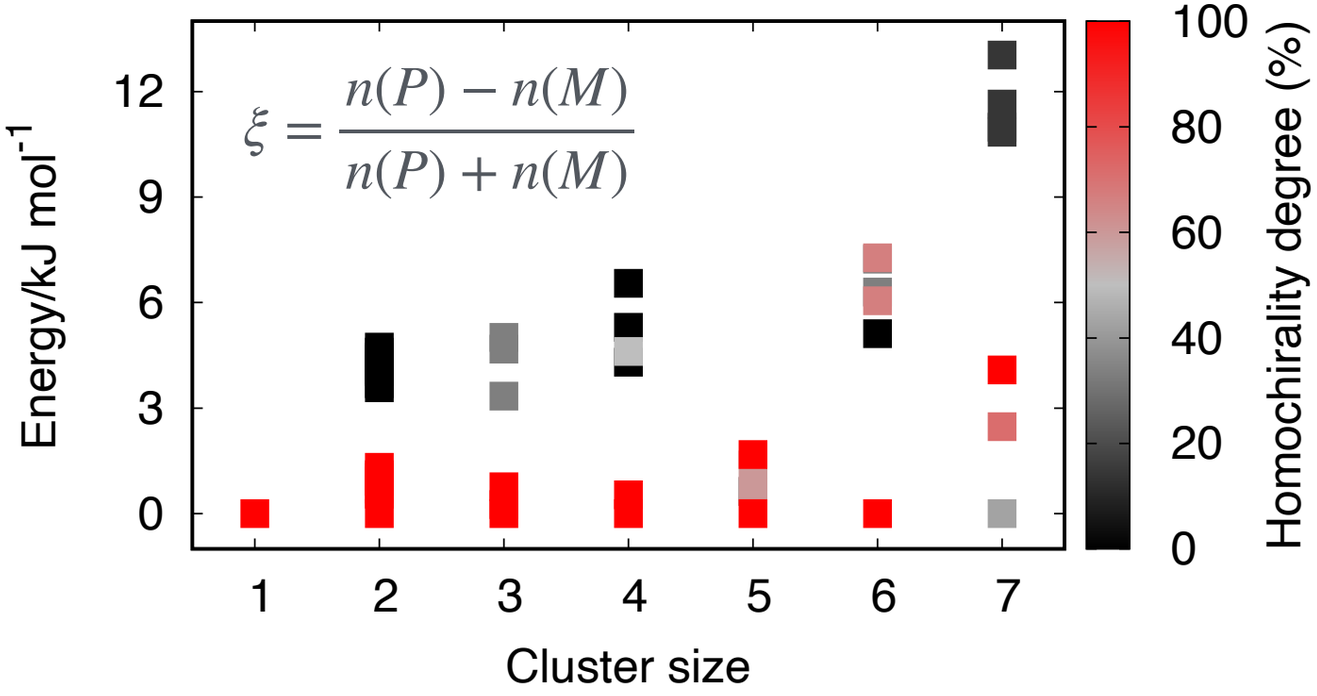


S(P) **S(P)** **R(P)** **S(P)** **S(P)**

Apparent bias in aggregation motifs observed.
4:1 for complexes predicted within 1 kJ/mol.

Clustering helicenes: is there break of symmetry?





Melanie Schnell and Denis Tikhonov (**DESY**)

Amanda Steber (**University of Valladolid**)

Laurent Nahon and Gustavo Garcia (**Synchrotron SOLEIL**)

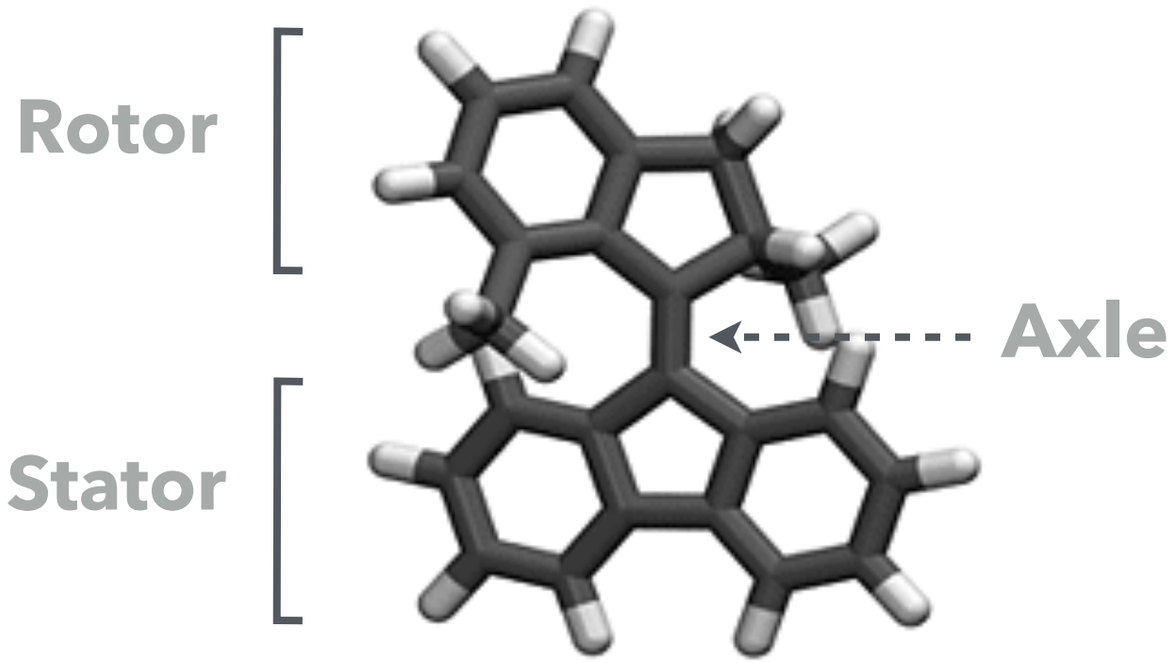
Narcis Avarvari (**University of Angers**)

Helgi R. Hrodmarsson (**LISA**)

Johannes Neugebauer (**University of Münster**)

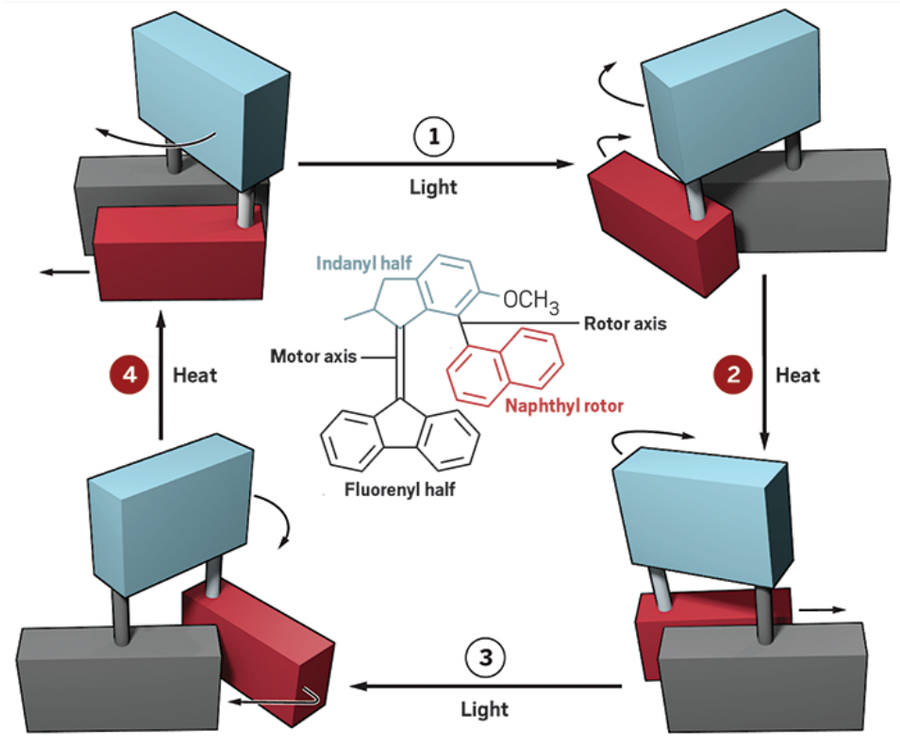
Domingos et al. **preprint *(2023).***

High resolution spectroscopy of Artificial Molecular Motors (AMM)

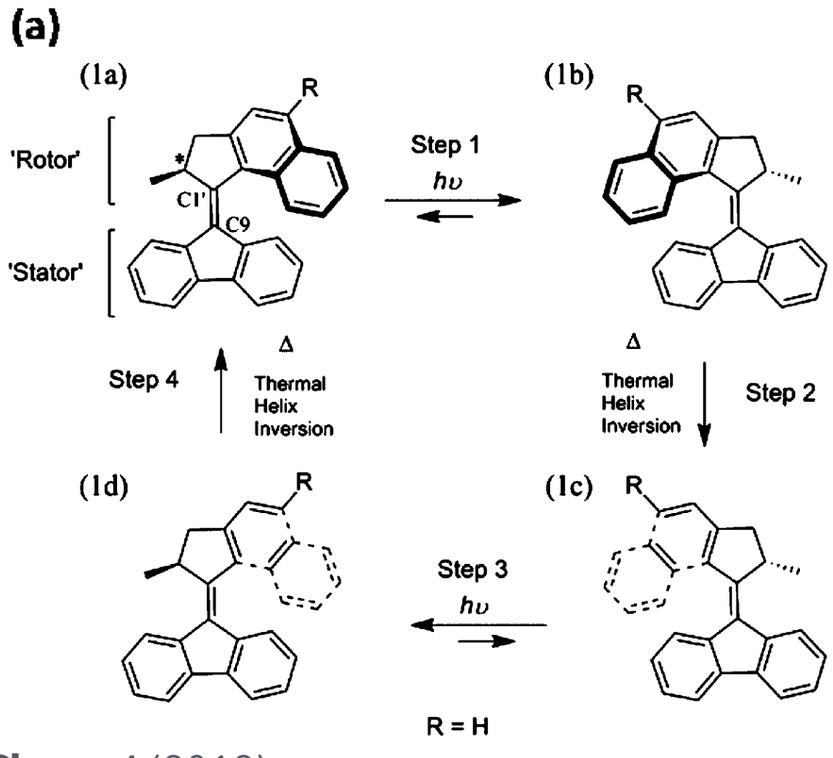


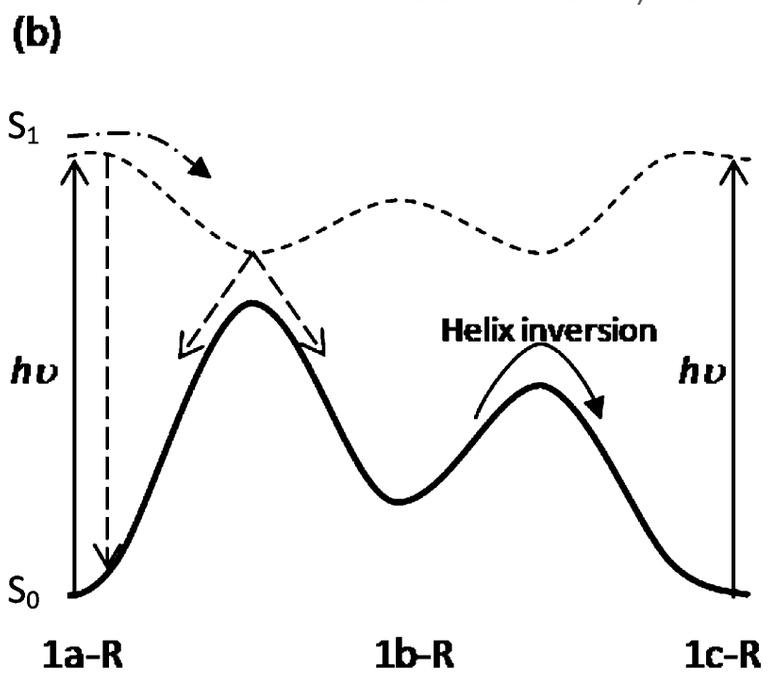
Ben Feringa & Wesley Browne

(University of Groningen, The Netherlands)



Štacko et al. *Science* ***356***, 964-968 (2017)





J. Conrad et al. **Nature Chem.** 4 (2012)

Structural Evolution of AMMs. Where we stand.

The rotational spectrum of the idle-mode of an AMM. $C_{27}H_{20}$

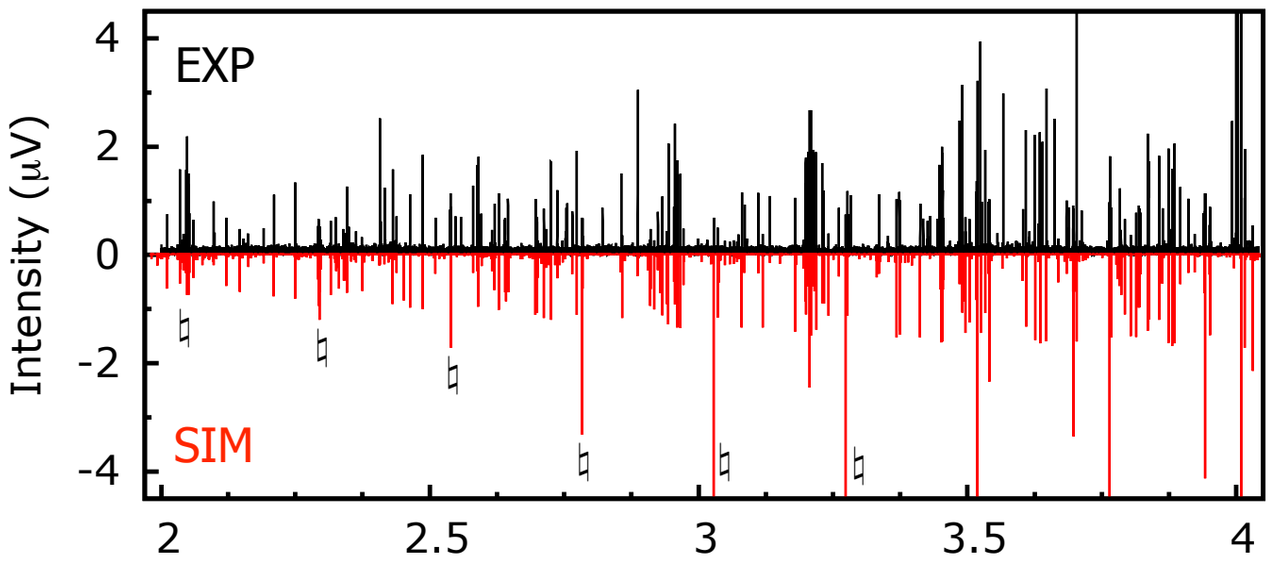
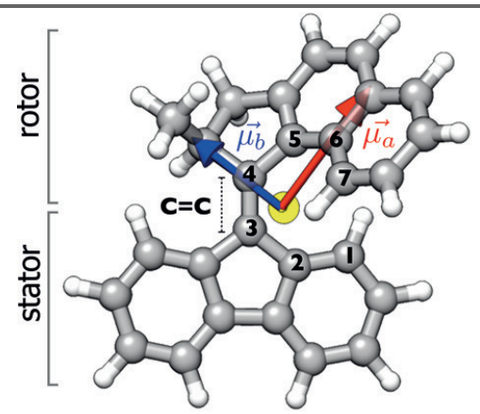


Table 1: Experimentally determined parameters for the vibronic ground state of the motor identified in the microwave spectrum.[a]

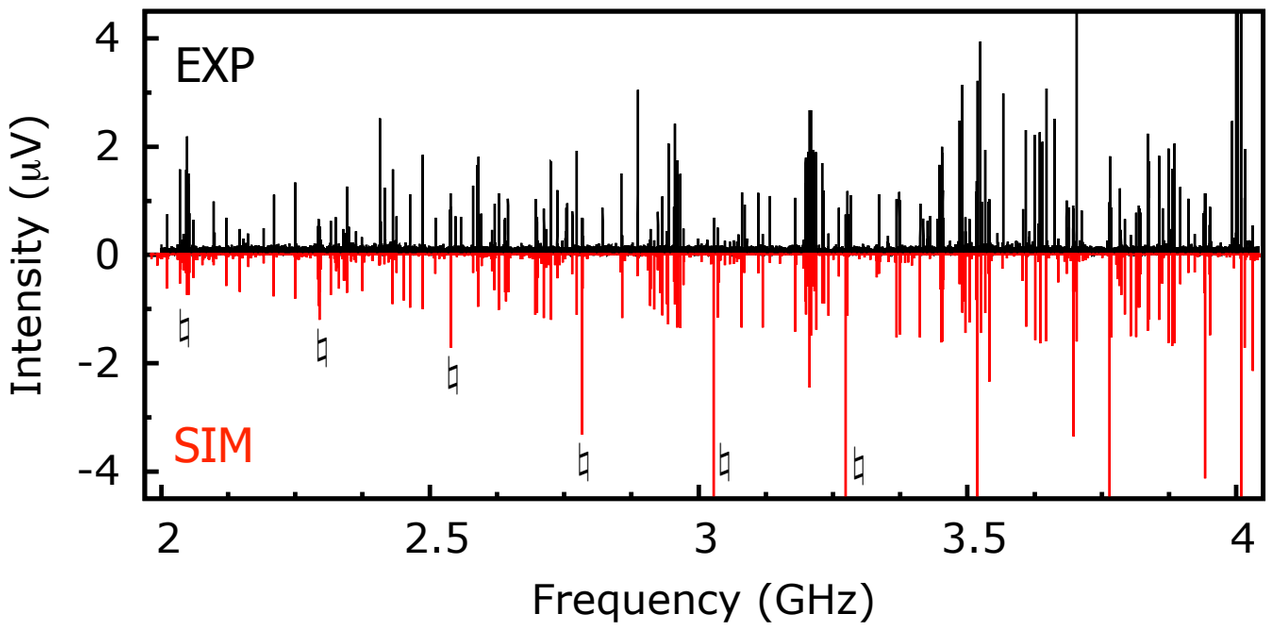
	Exp.		B3LYP-D3BJ[c]
A [MHz]	307.183437(46)		308.633
B [MHz]	164.951398(47)		166.282
C [MHz]	122.506084(33)		122.875
D_J [kHz]	0.001431(90)		–
d_J [kHz]	0.000271(50)		–
$\lvert\mu_a\rvert$ [D]	y		1.37
$\lvert\mu_b\rvert$ [D]	y		0.99
$\lvert\mu_c\rvert$ [D]	n		0.11
N	222		–
σ [kHz]	3.4		–
κ	−0.540		−0.532

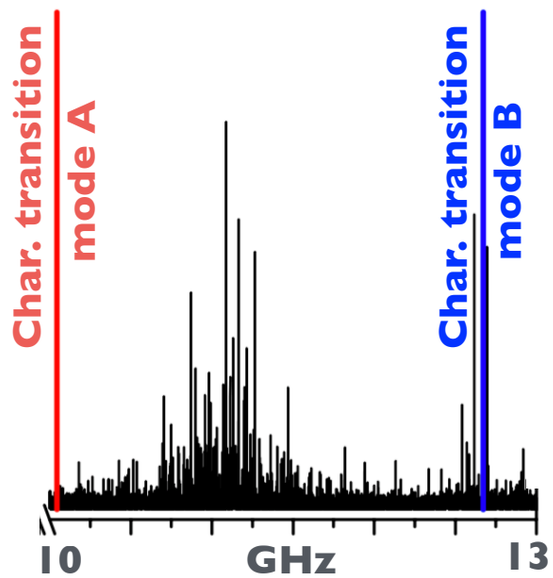
[a] Rotational constants (*A*, *B*, *C* in MHz) and quartic centrifugal distortion constants (in kHz); type of spectrum observed (a-type, b-type, c-type) with y being observed and n being not observed; predicted dipole moments; number of lines used in the fit; standard error of the fit (in kHz); asymmetry parameter $\kappa = (2B\text{-}A\text{-}C)/(A\text{-}C)$. The experimental frequency accuracy is 25 kHz. [b] 6-311++G** basis set. [c] def2-TZVP basis set.

SRD, A. Cnossen, W.J. Buma, W.R. Browne, B.L. Feringa, M. Schnell ***Angew. Chem. Int. Ed.*** 56, 11209-11212. (2017)

Structural Evolution of AMMs. Where we stand. Where we're going.

The rotational spectrum of the idle-mode of an AMM. $C_{27}H_{20}$





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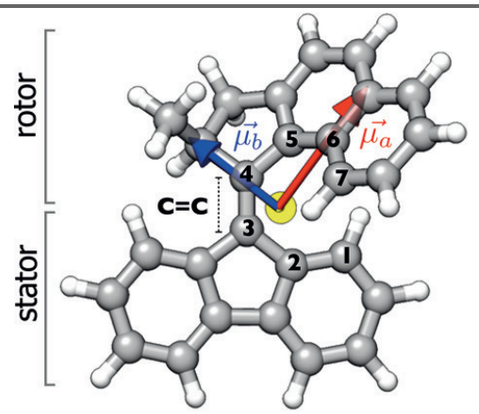
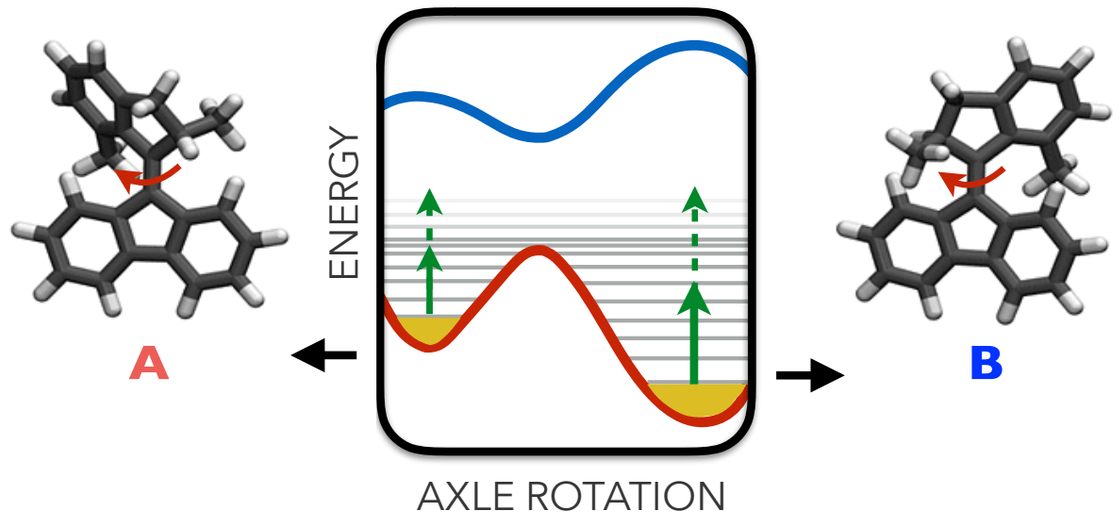
D_J [kHz]	0.001431(90)		–
d_J [kHz]	0.000271(50)		–
$\lvert\mu_a\rvert$ [D]	y		1.37
$\lvert\mu_b\rvert$ [D]	y		0.99
$\lvert\mu_c\rvert$ [D]	n		0.11
N	222		–
σ [kHz]	3.4		–
κ	−0.540		−0.532

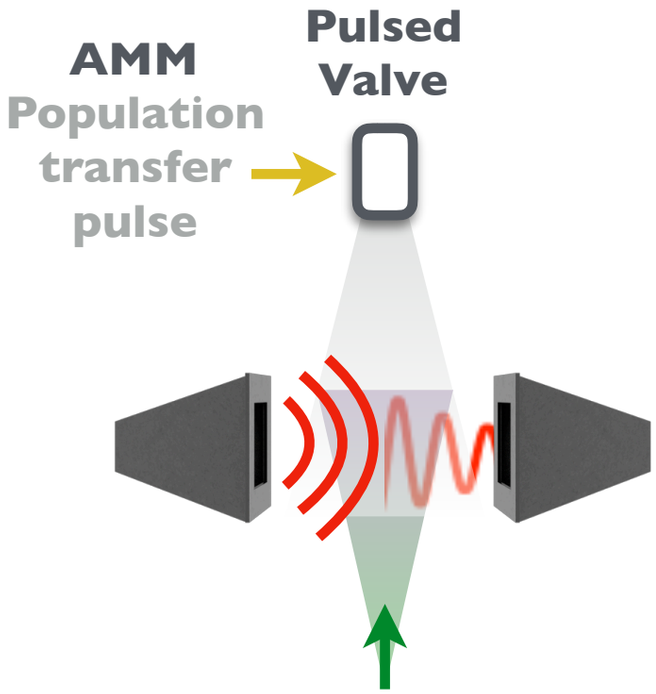


[a] Rotational constants (A, B, C in MHz) and quartic centrifugal distortion constants (in kHz); type of spectrum observed (a-type, b-type, c-type) with y being observed and n being not observed; predicted dipole moments; number of lines used in the fit; standard error of the fit (in kHz); asymmetry parameter $\kappa = (2B\text{-}A\text{-}C)/(A\text{-}C)$. The experimental frequency accuracy is 25 kHz. [b] 6-311++G** basis set. [c] def2-TZVP basis set.

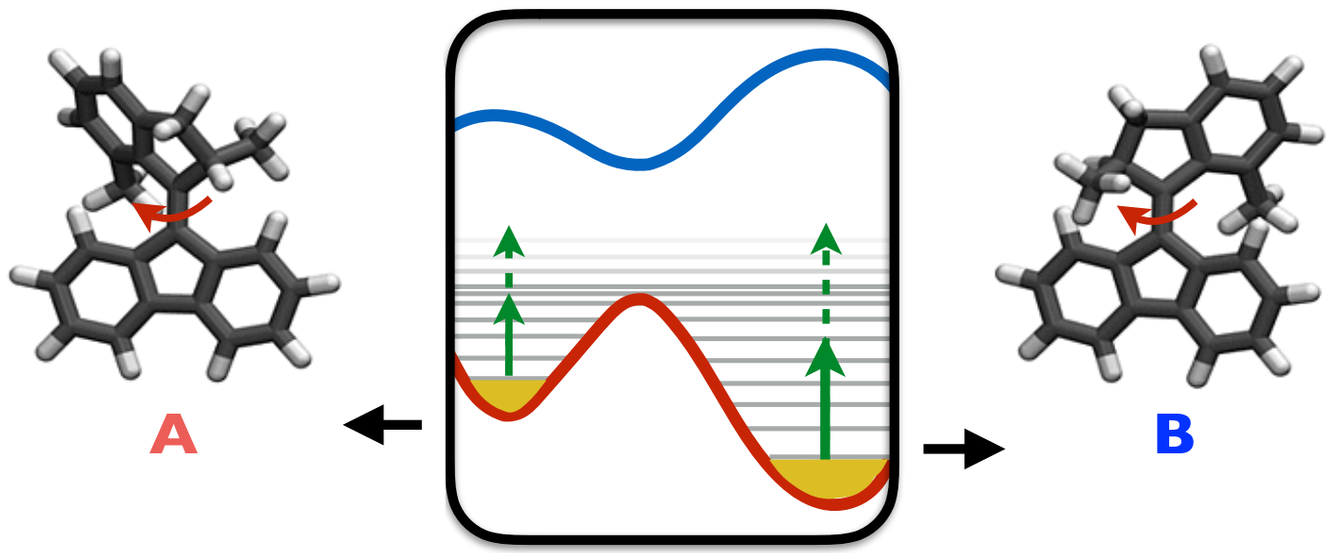


SRD, A. Cnossen, W.J. Buma, W.R. Browne, B.L. Feringa, M. Schnell ***Angew. Chem. Int. Ed.*** 56, 11209-11212. (2017)

Structural Evolution of AMMs. Follow up challenges?



AMM
Isomerization
IR pulse



Summary | Future work | **Take home message**

- We can learn much on **structure-function relations** from rich, dense, conformationally-sensitive broadband **rotational spectra**.

Summary | Future work | Take home message

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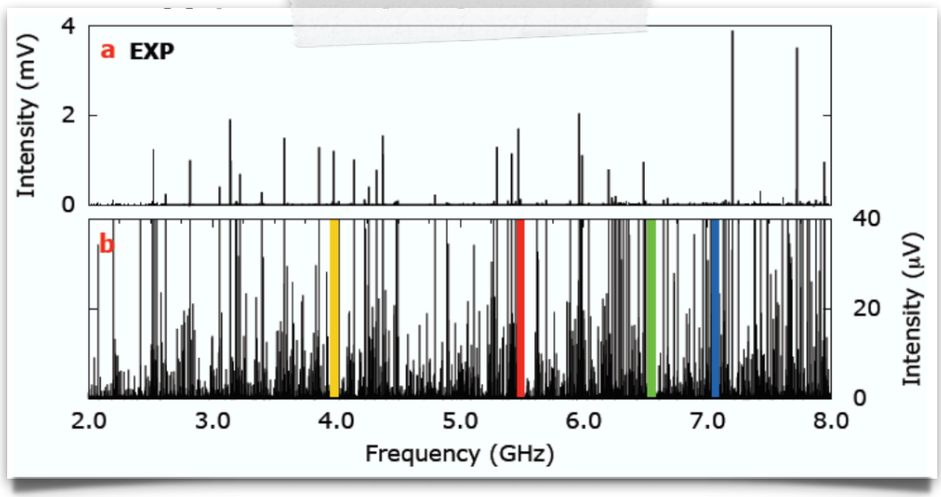

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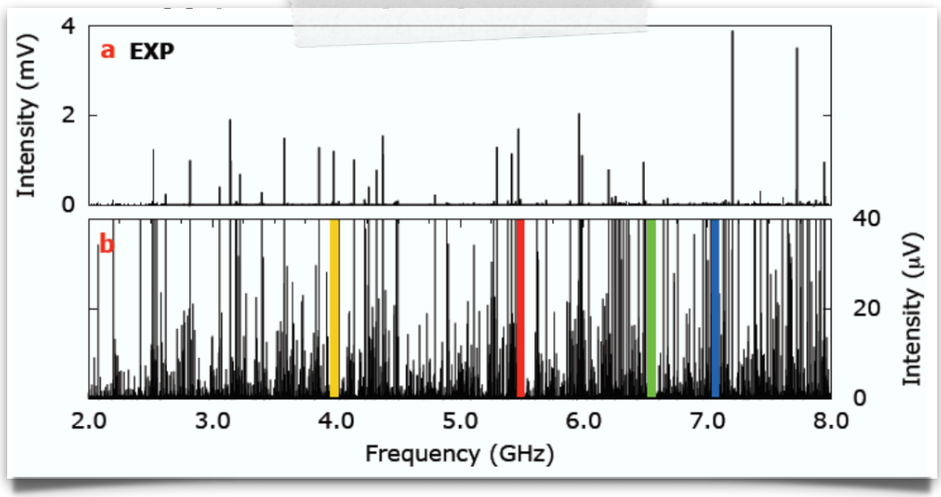

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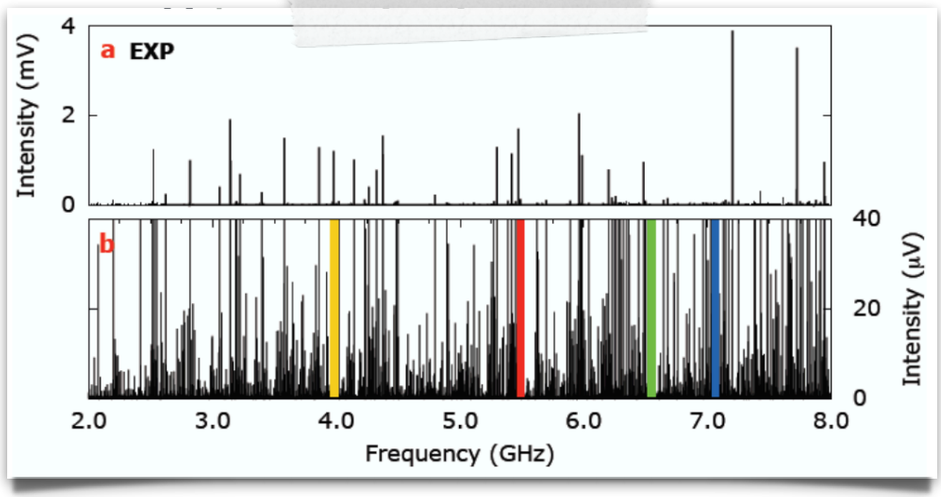

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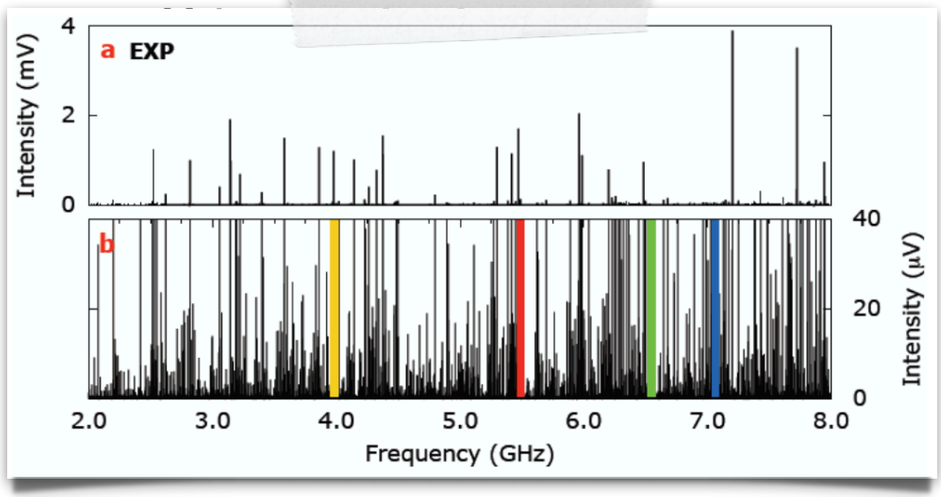

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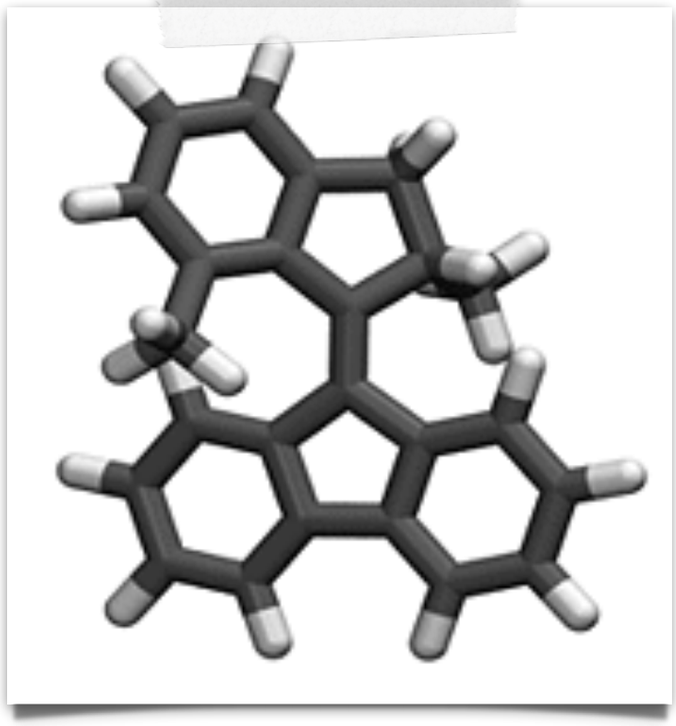
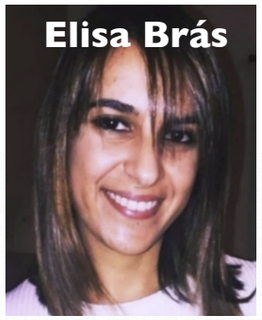


- Can we reliably **extract dynamic information** from rotational spectra, in particular from large and complex molecular species such as **AMMs**?

Spectroscopy & Molecular Physics **Group @** CFisUC



Collaborators

Melanie Schnell
Deutsches Elektronen-Synchrotron

Cristóbal Pérez
University of Valladolid

Christian Merten
Ruhr University Bochum

Narcis Avarvari
Angers University

Mark D. Marshall
Helen O. Leung
Amherst Colleague MA

Ben L. Feringa
Wesley R. Browne
University of Groningen

Wybren Jan Buma
University of Amsterdam

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