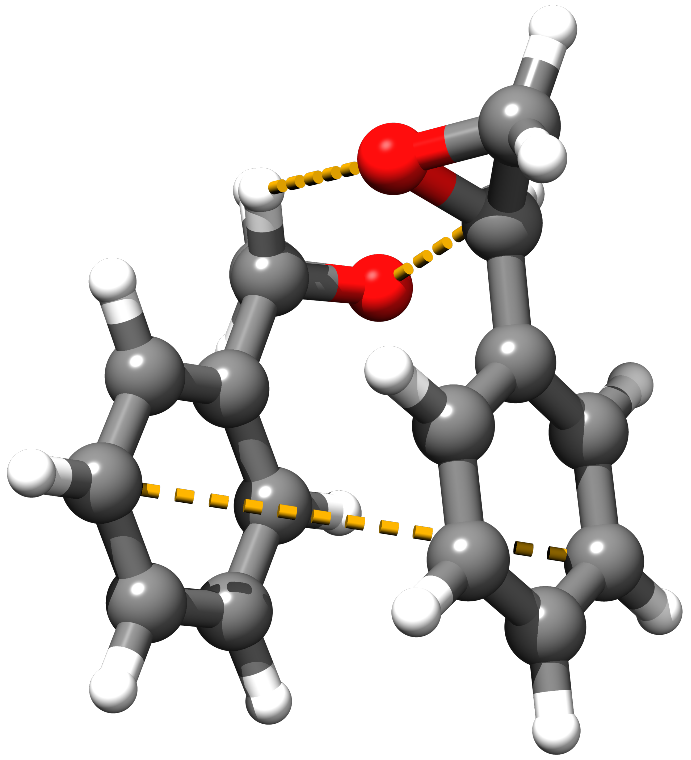
The styrene oxide story

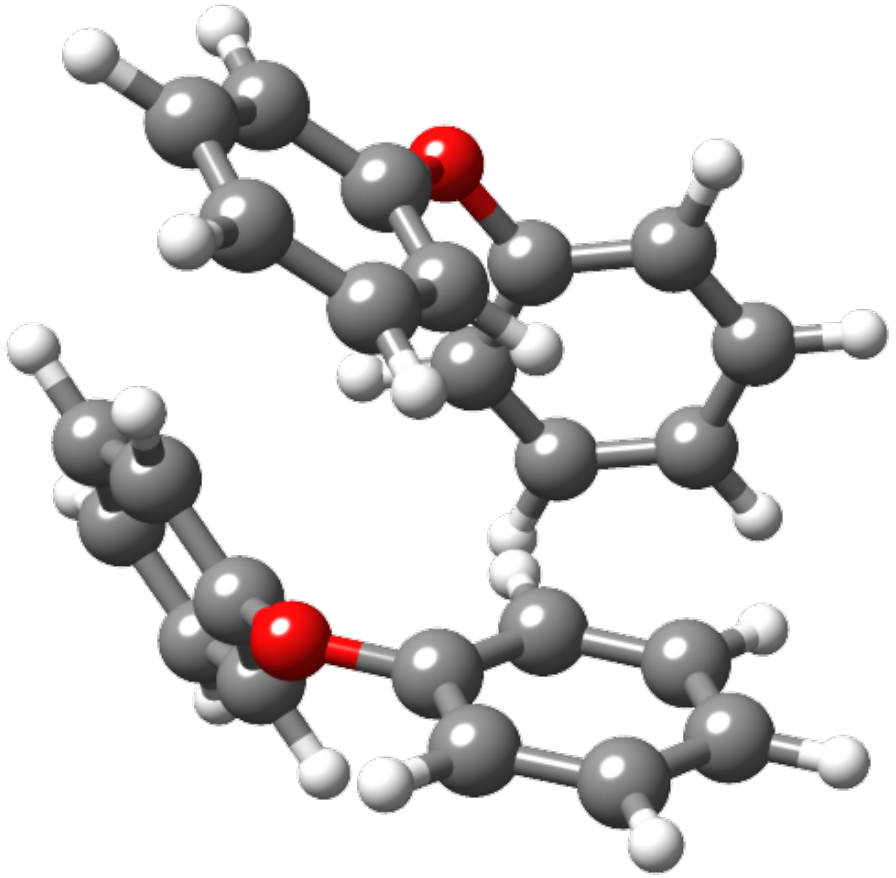
Sergio R. Domingos
Melanie Schnell



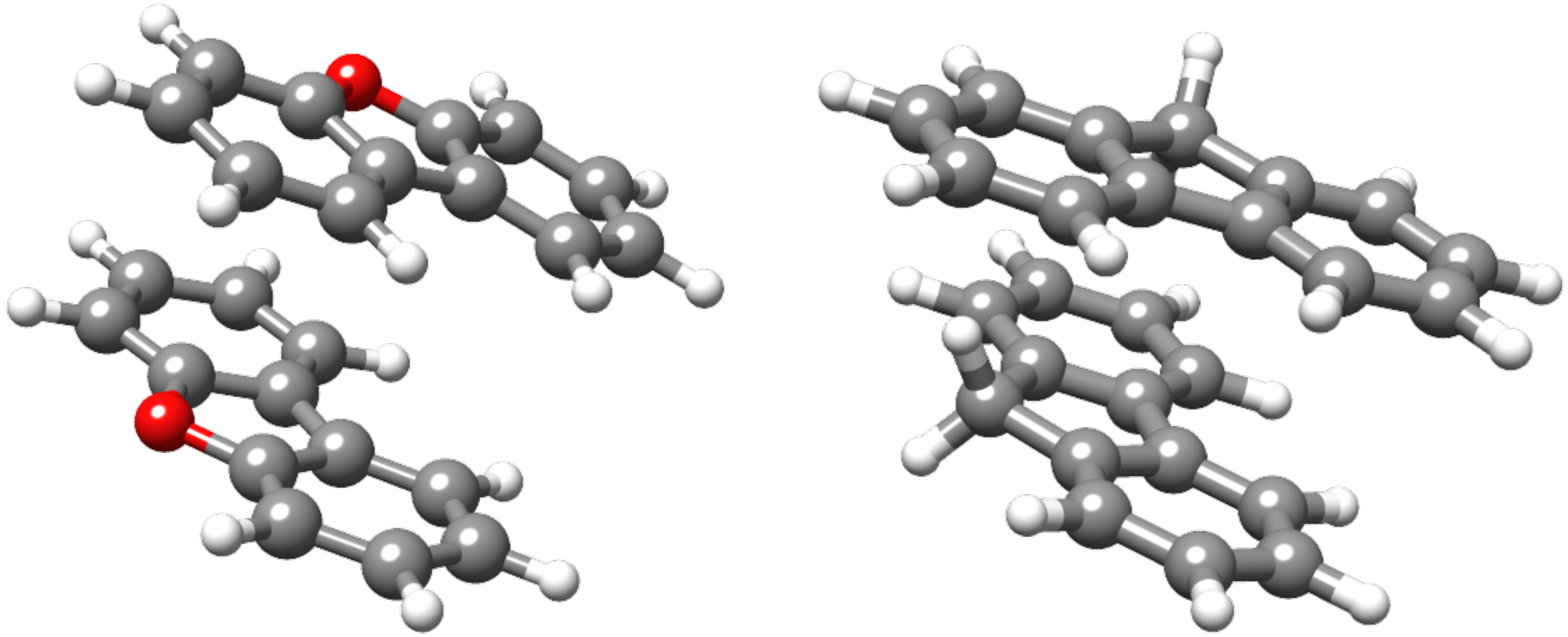
Hierarchy of intermolecular interactions

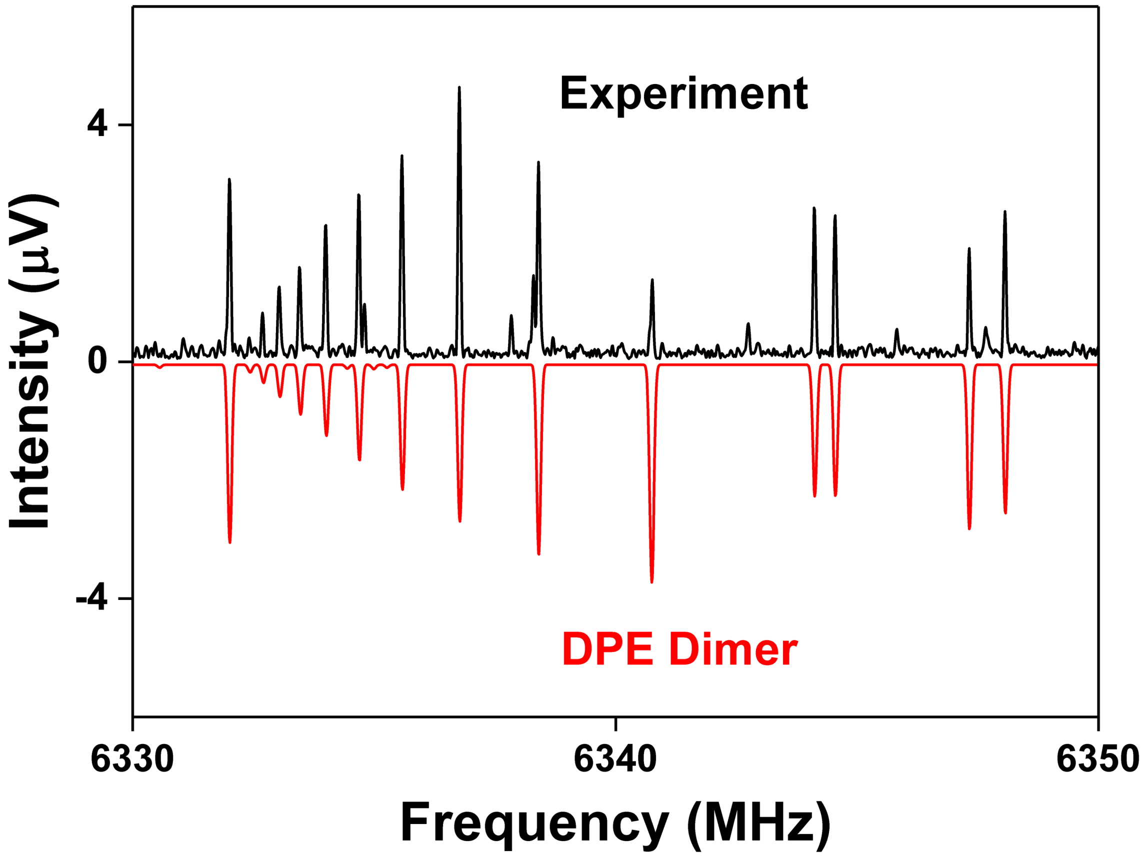
Dispersion vs. hydrogen bonding

C-H — π bonding



$\pi - \pi$ bonding

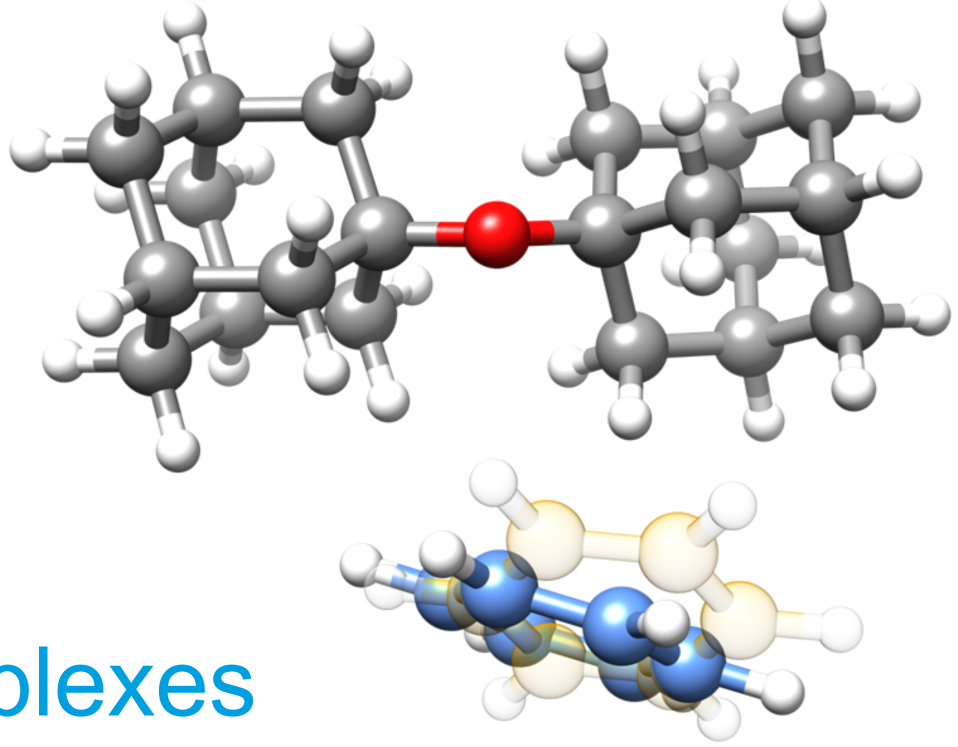




M. Fatima, A. L. Steber, A. Poblotzki, C. Perez, M. Schnell,
Angewandte Chemie Int. Ed. accepted (2019).

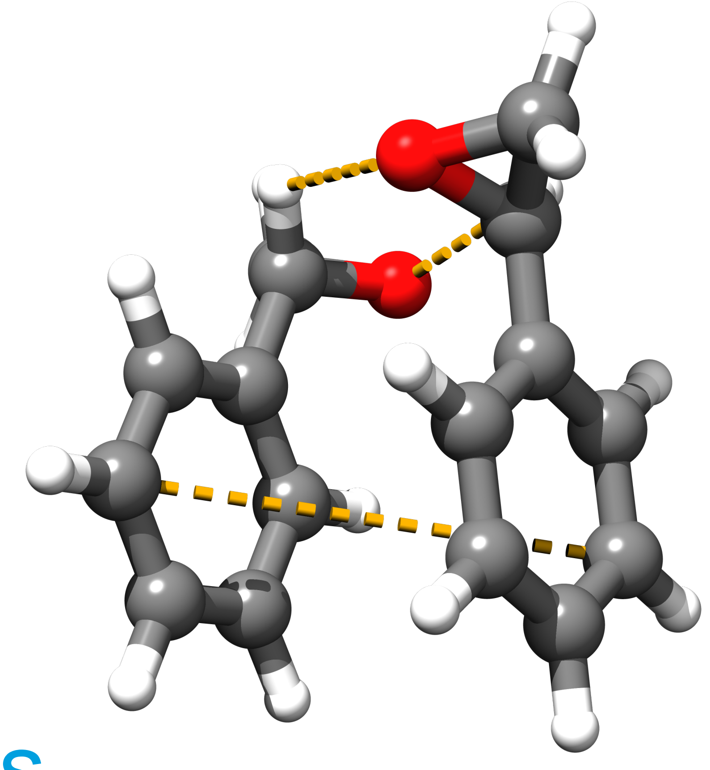
Intermolecular interactions.

- **interplay between intermolecular interactions (H bonds vs. dispersion)**



diadamantyl ether complexes

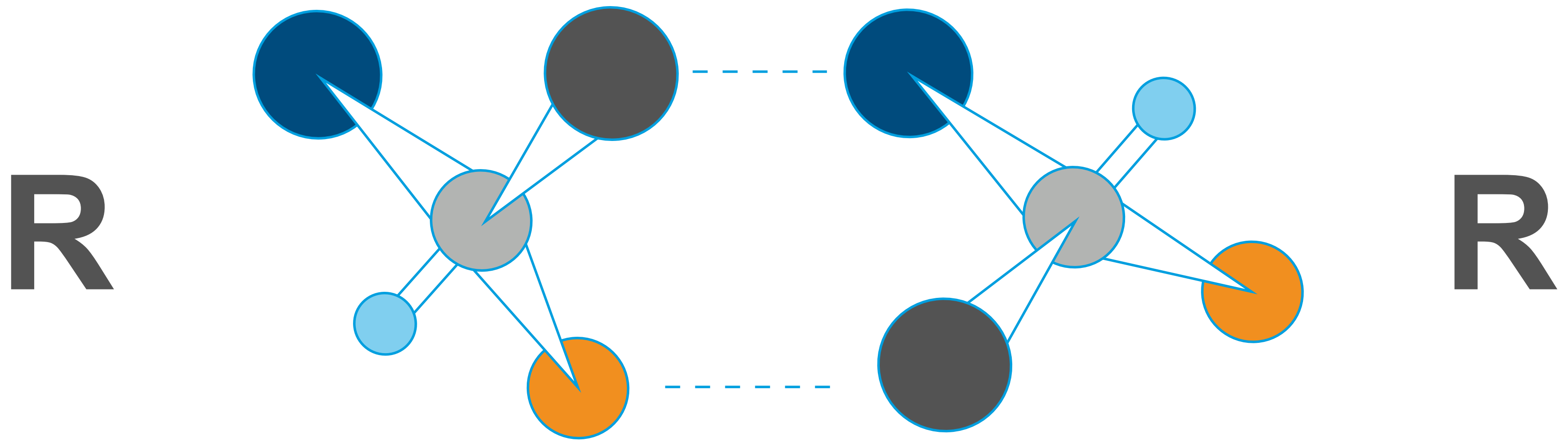
- **homo- vs. heterochirality - towards an analytical tool**

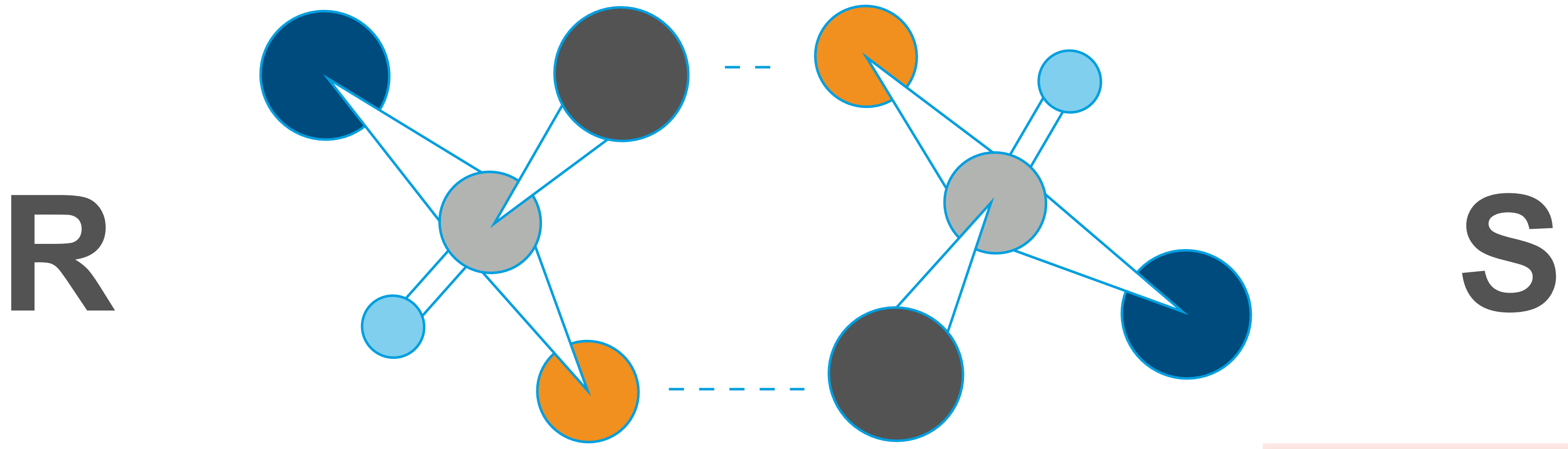


styrene oxide dimers

Dispersion and chirality.

SPP 1807
Dispersion





Chiralität

DOI: 10.1002/ange.200800957

Chiralitätserkennung zwischen neutralen Molekülen in der Gasphase

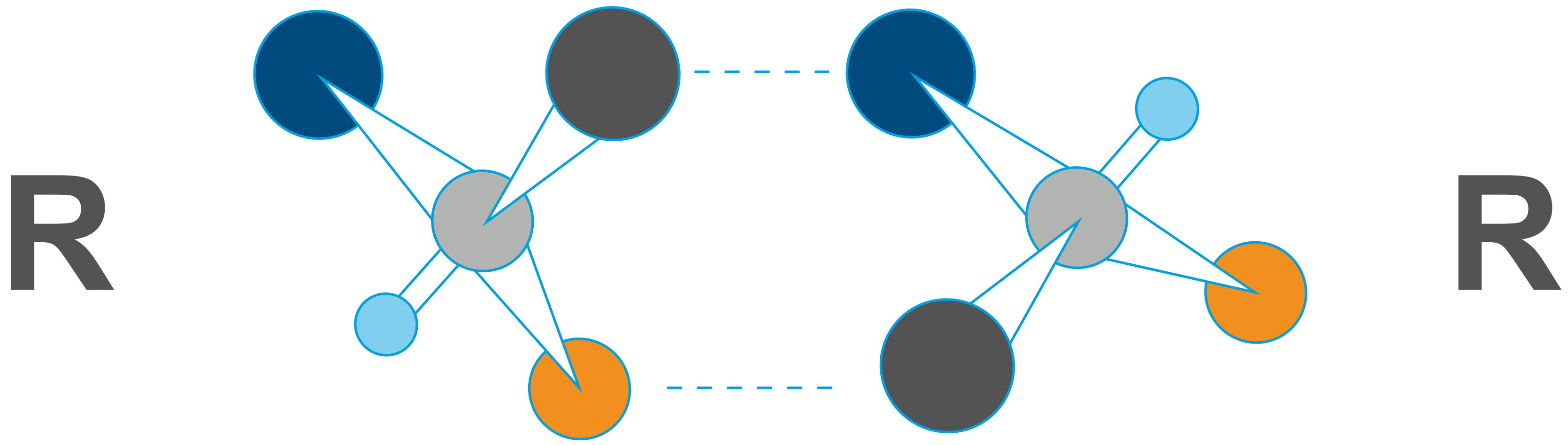
Anne Zehnacker und Martin A. Suhm**

Diastereomer formation

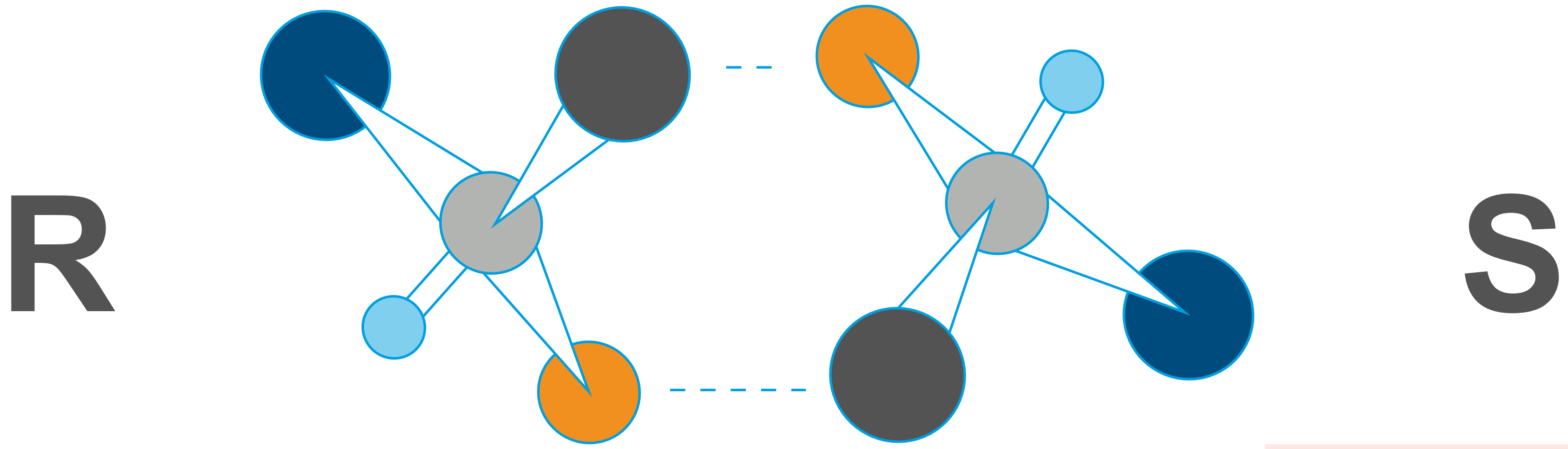
↓

different rotational spectra

Dispersion and chirality.



HYDROGEN BONDING?



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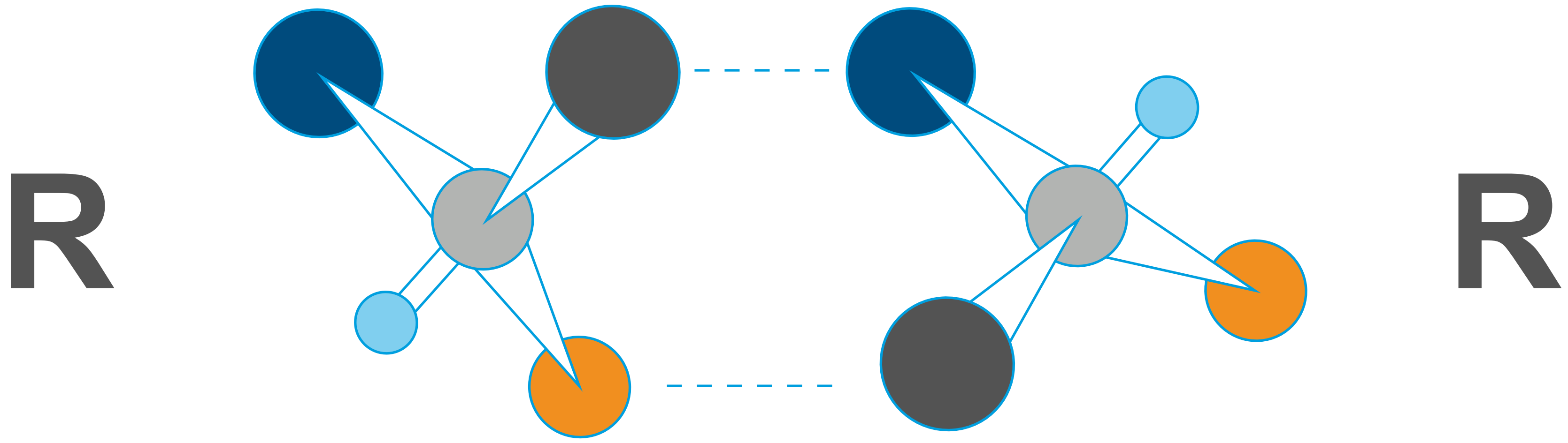
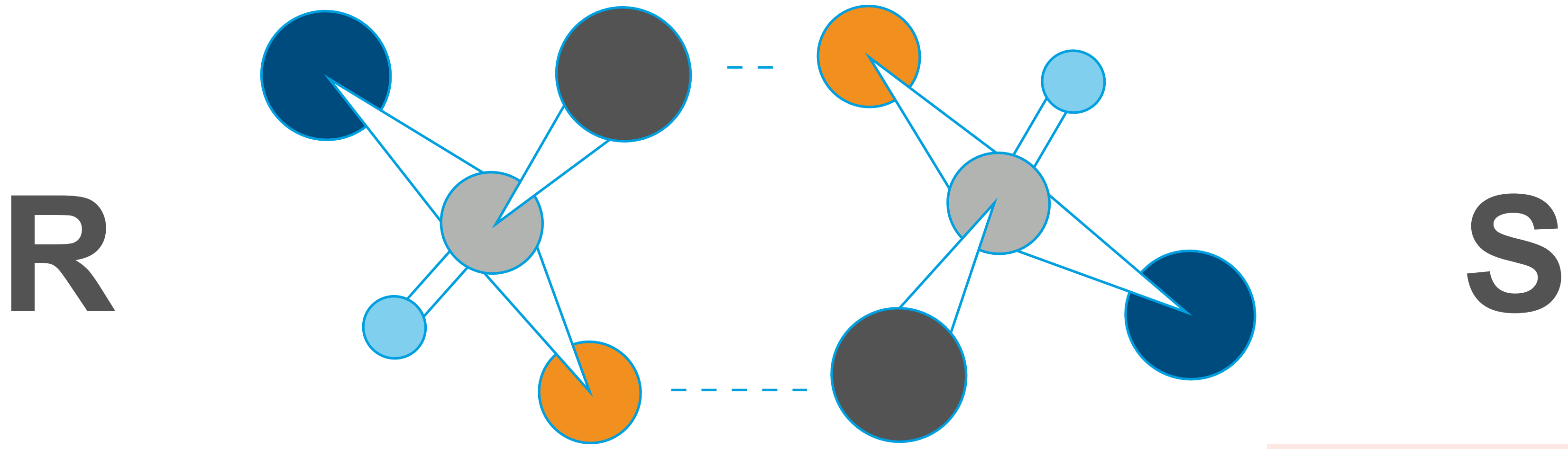


DISPERSION FORCES?



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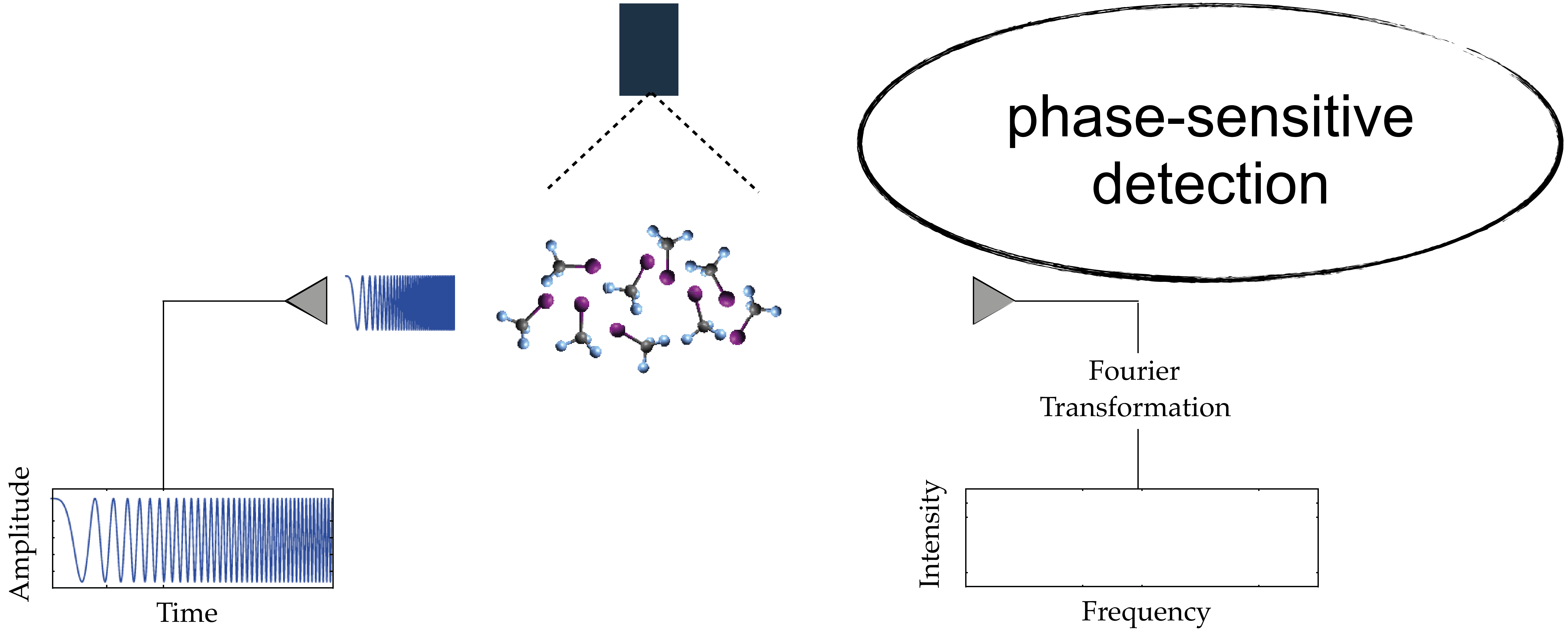
The broadband chirp technique

Experimental procedure: broadband rotational spectroscopy

- covers a wide frequency range within *a single acquisition* (in Hamburg: 2-18 GHz, 18-26 GHz, 75-110 GHz,)
- robust technique, high resolution (25 kHz)
- molecules need a dipole moment



phase-sensitive detection

Fourier Transformation

D. Schmitz, V.A. Shubert, T. Betz, M. Schnell, *J. Mol. Spectrosc.* **280** (2012) 77.

G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman, B. H. Pate *Rev. Sci. Instrum.* **79** (2008) 053103.

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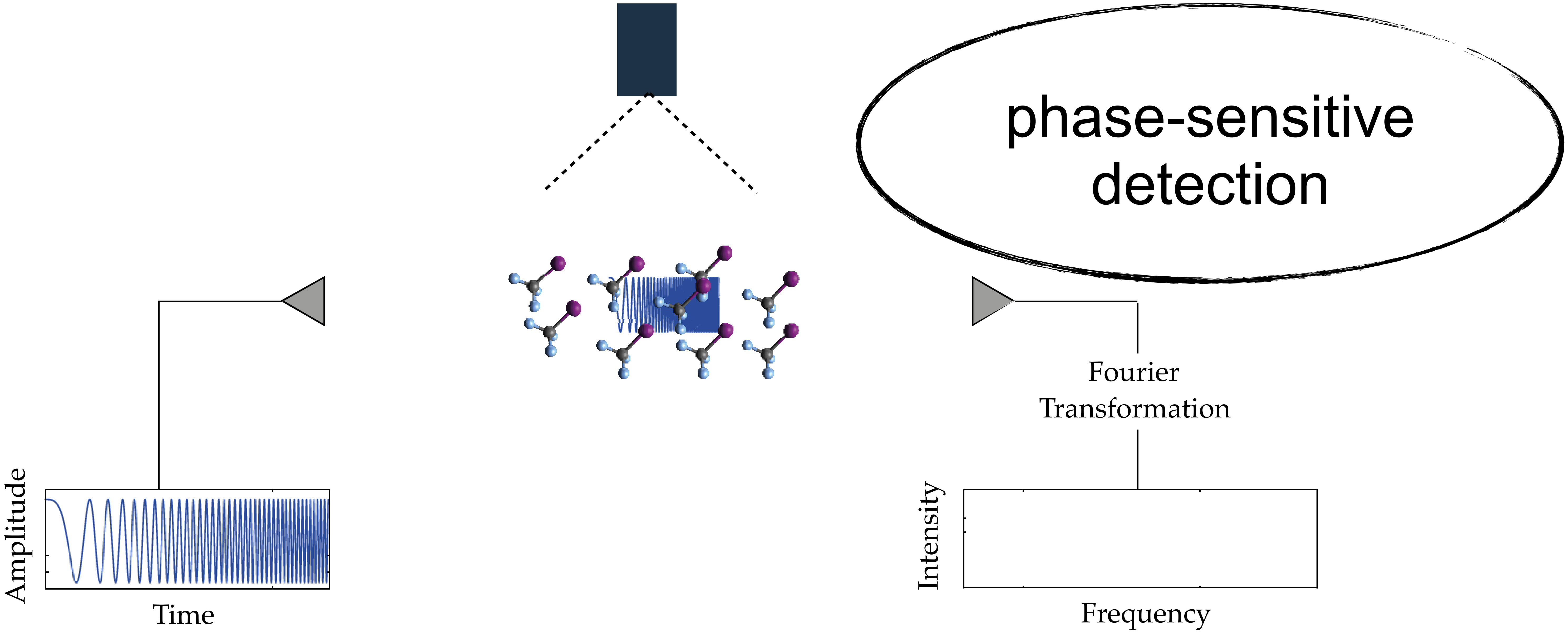

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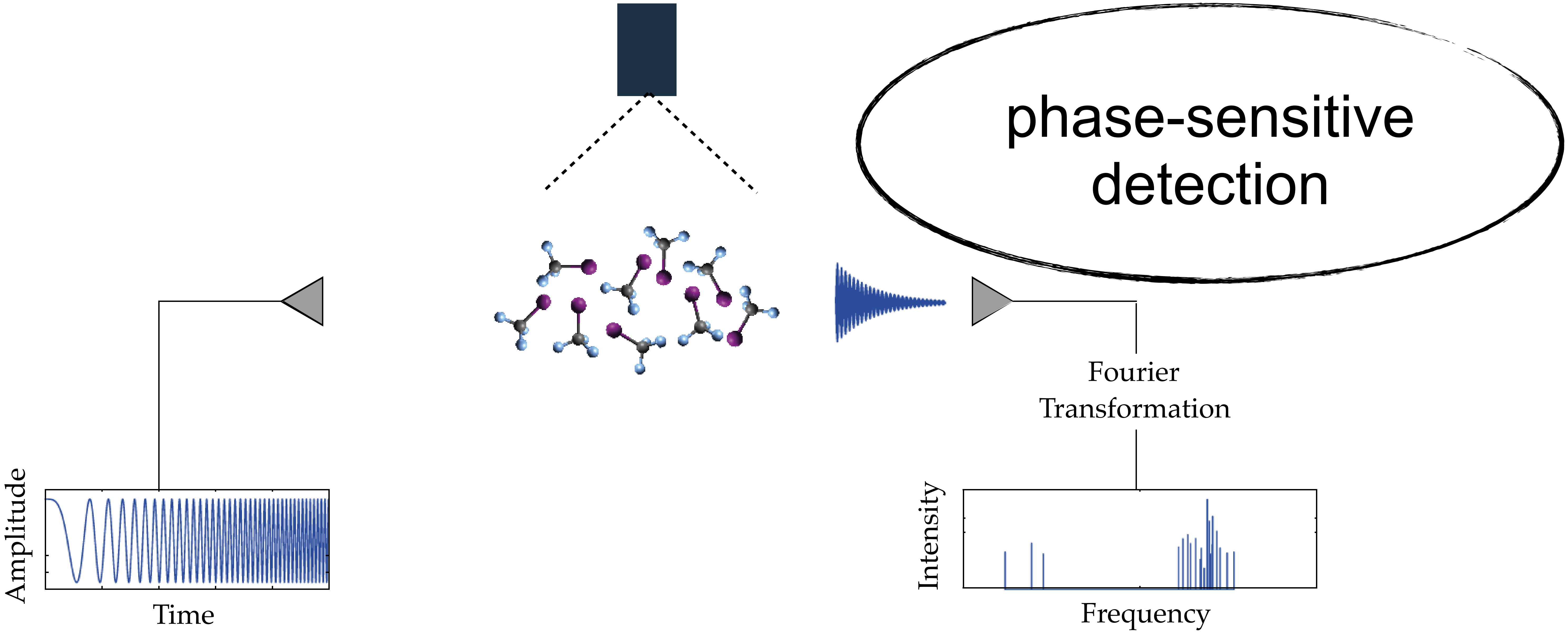

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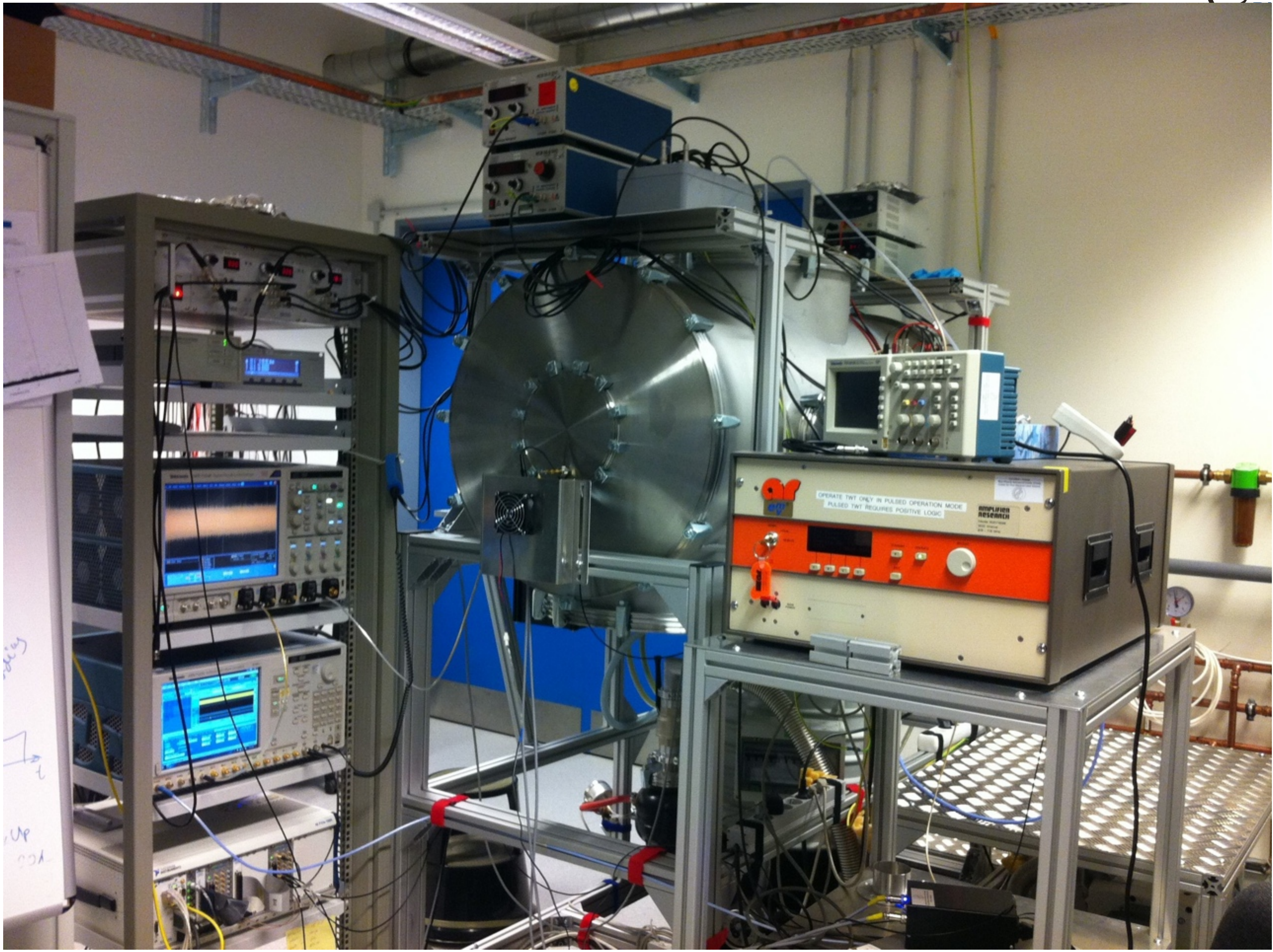
The Hamburg COMPACT spectrometer

SPP 1807
spersion

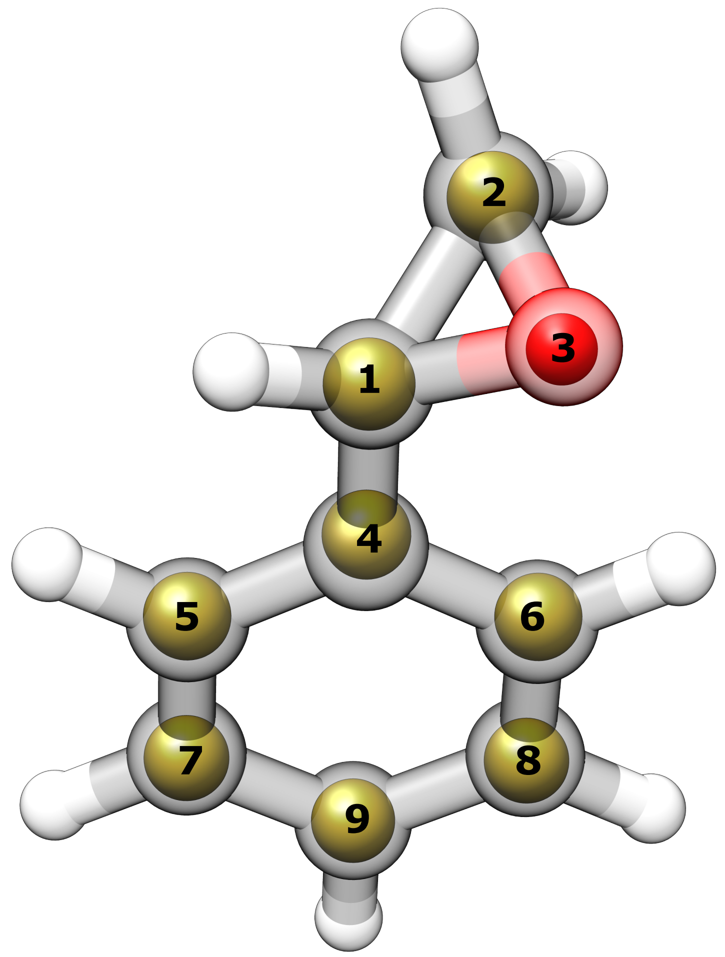


DESY.

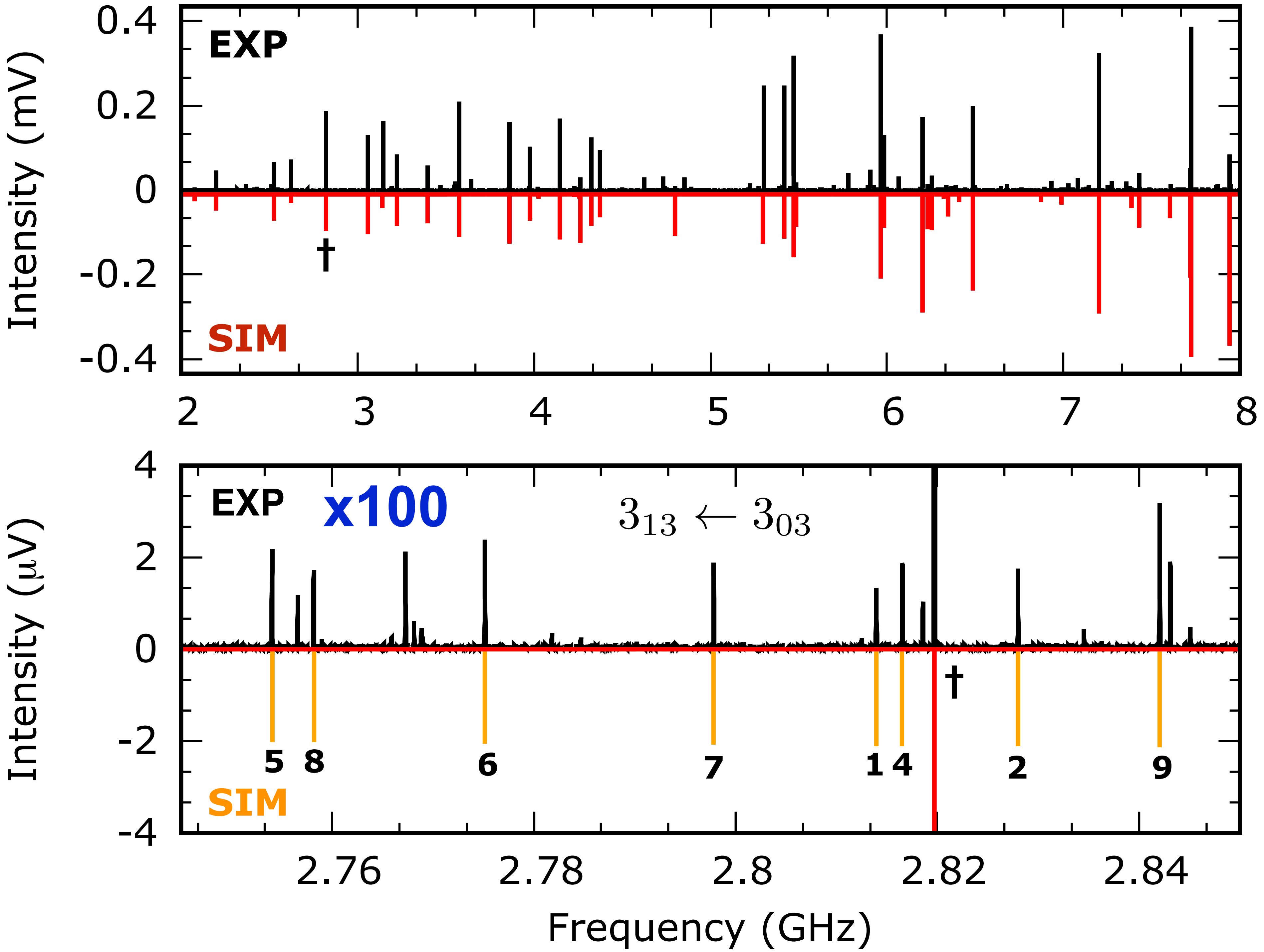
D. Schmitz, V.A. Shubert, T. Betz, M. Schnell, *J. Mol. Spectrosc.* **280** (2012) 77.

Monomer rotational spectrum.

Including isotopologues in natural abundance



Styrene oxide



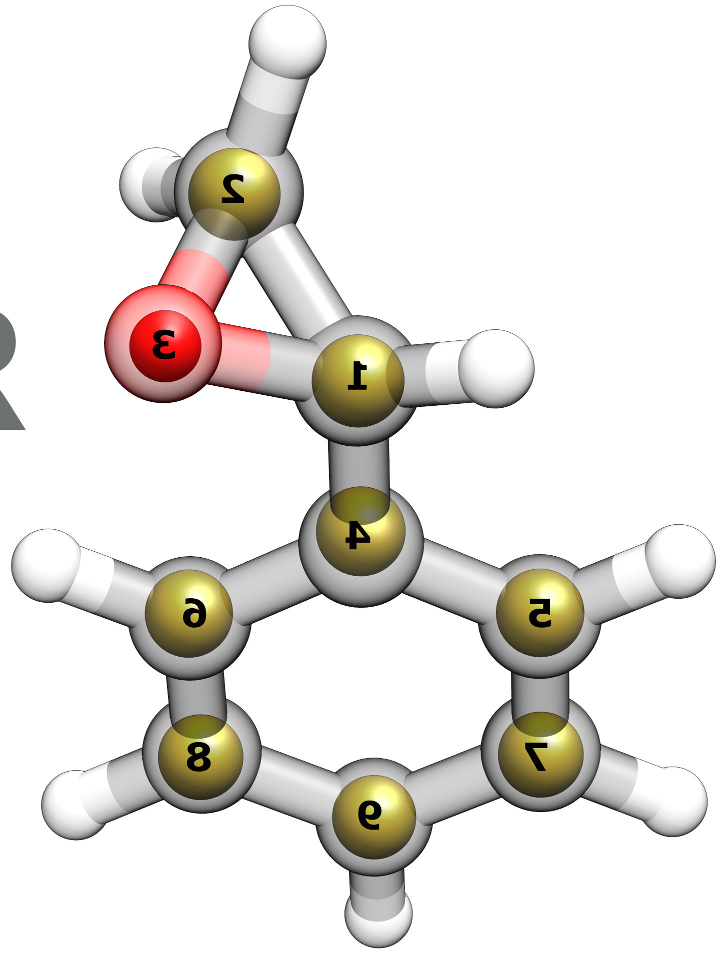
	Expt.	B3LYP-D3(BJ)[a]
A/MHz	4348.86437(99)	4392.96
B/MHz	1124.88255(30)	1125.15
C/MHz	951.22618(24)	952.62
D_J/kHz	0.0485(27)	-
D_{JK}/kHz	0.151(19)	-
D_K/kHz	0.528(36)	-
d_J/kHz	0.00840(55)	-
d_K/kHz	−0.512(37)	-
$\lvert\mu_a\rvert$	y	0.6
$\lvert\mu_b\rvert$	y	1.0
$\lvert\mu_c\rvert$	y	1.3
N	ca 70	-
σ/kHz	5.5	-

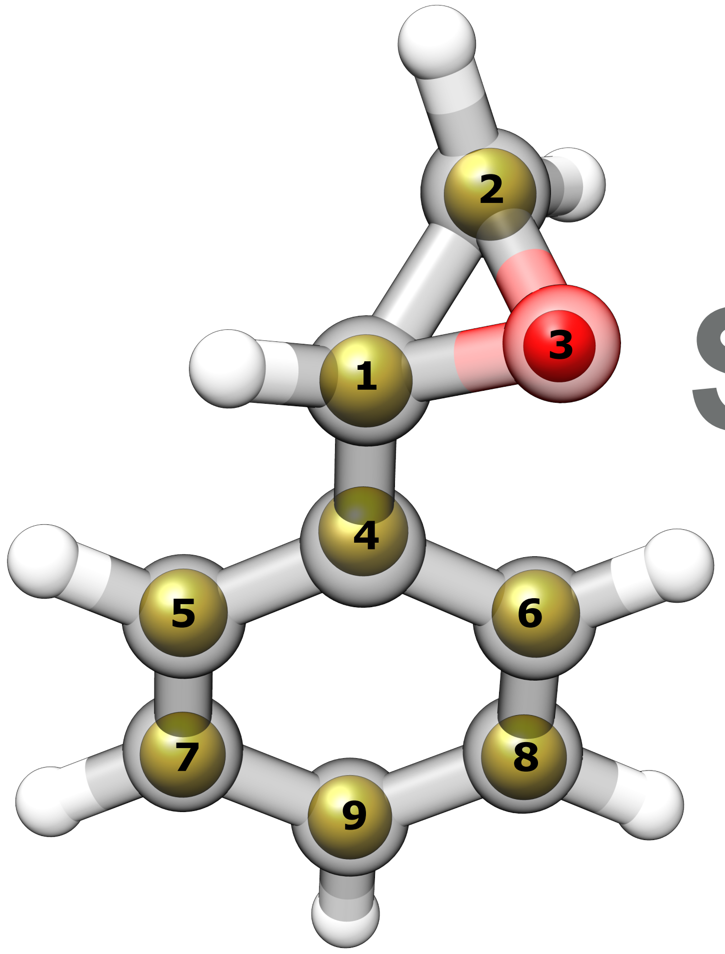
[a] def2-tzvp basis set

Chiral pairing.

Probing diastereomers using rotational spectroscopy

R





S

RR RS SR SS

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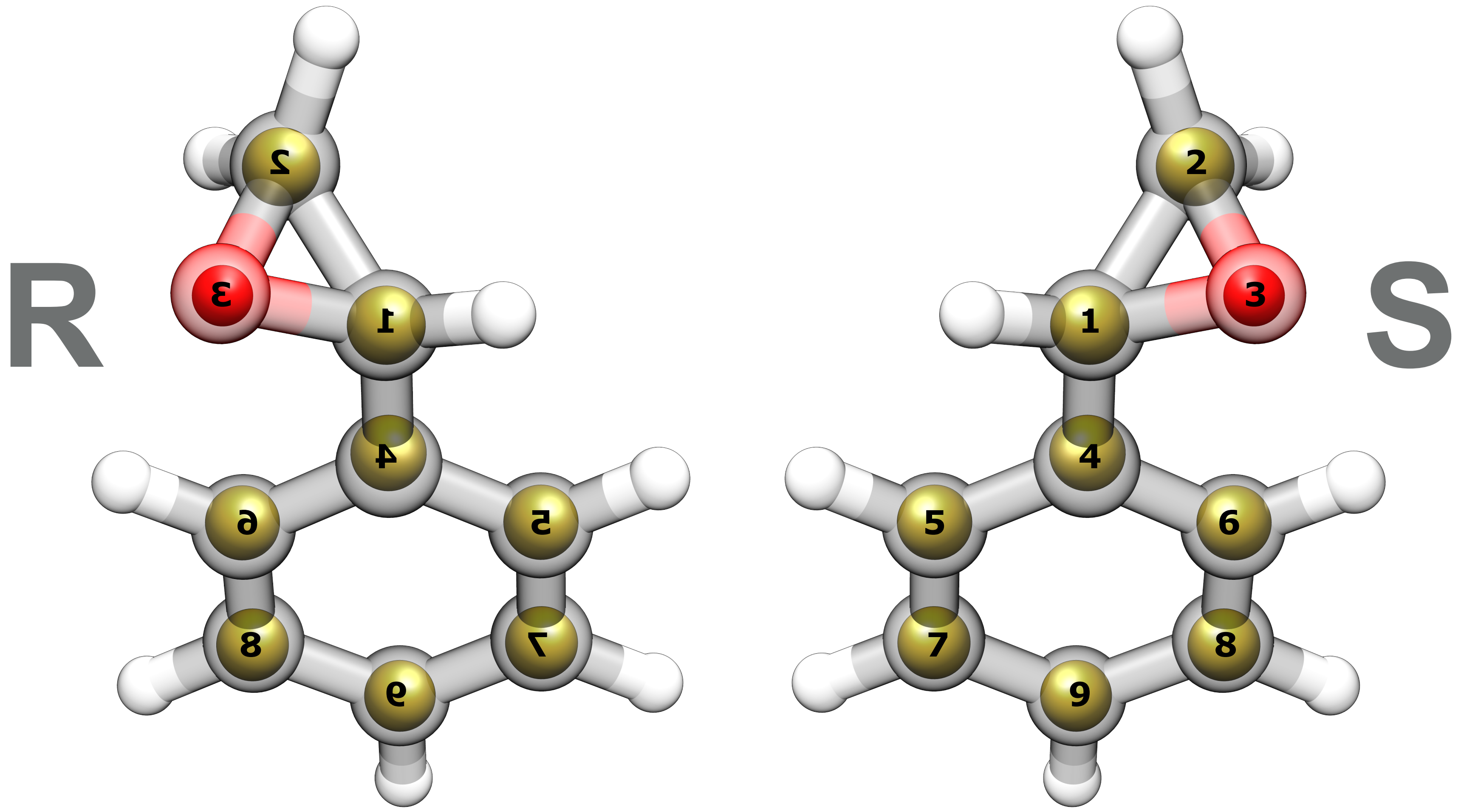
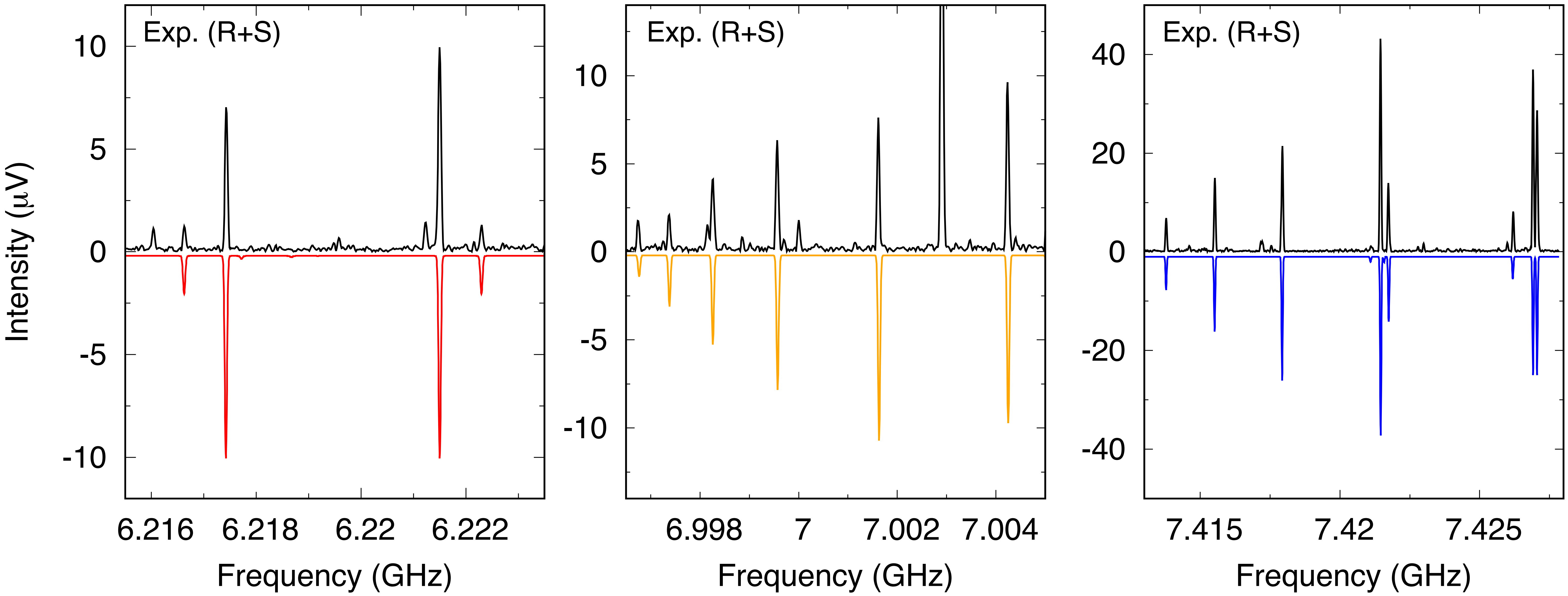


RR **RS** **SR** **SS**

The styrene oxide dimers.

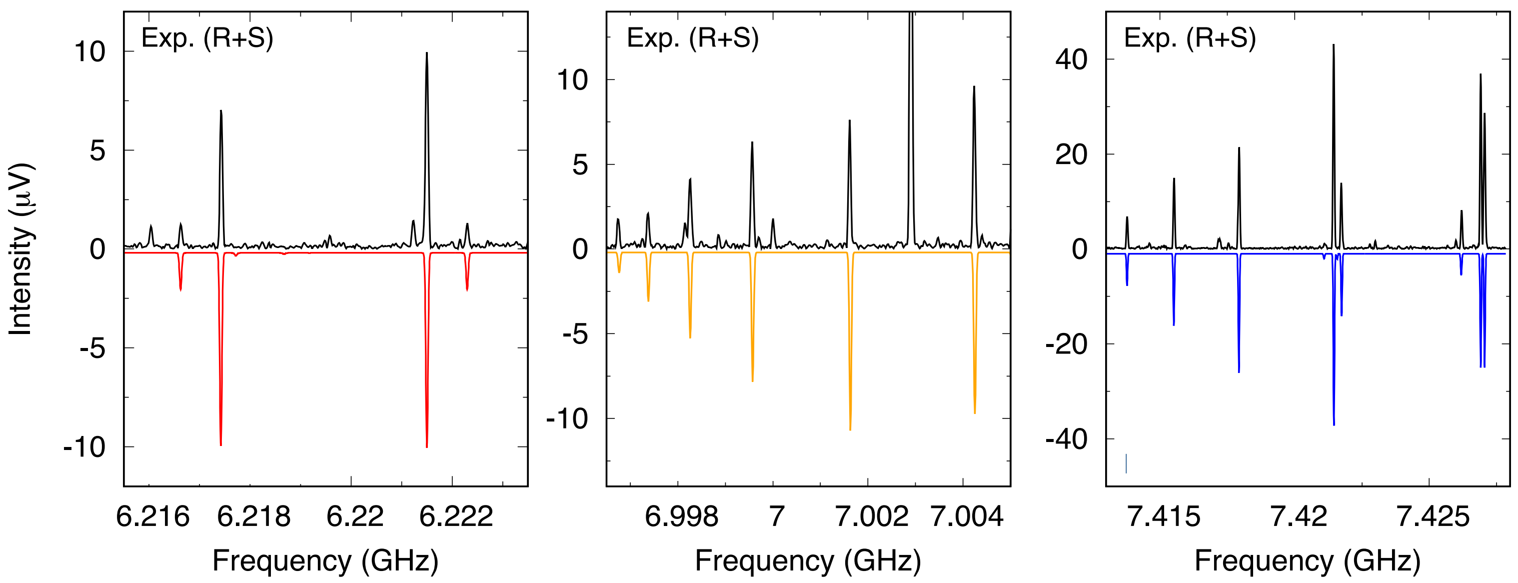
Rotational spectra using a racemic sample



A **565.13225(13) MHz**	**A** **476.41136(25) MHz**	**A** **519.837930(80) MHz**
B **327.768166(84) MHz**	**B** **399.70557(17) MHz**	**B** **350.271868(52) MHz**
C **307.883749(90) MHz**	**C** **371.57733(16) MHz**	**C** **322.618173(56) MHz**

Preferences of chiral aggregation.

Homochiral vs Heterochiral



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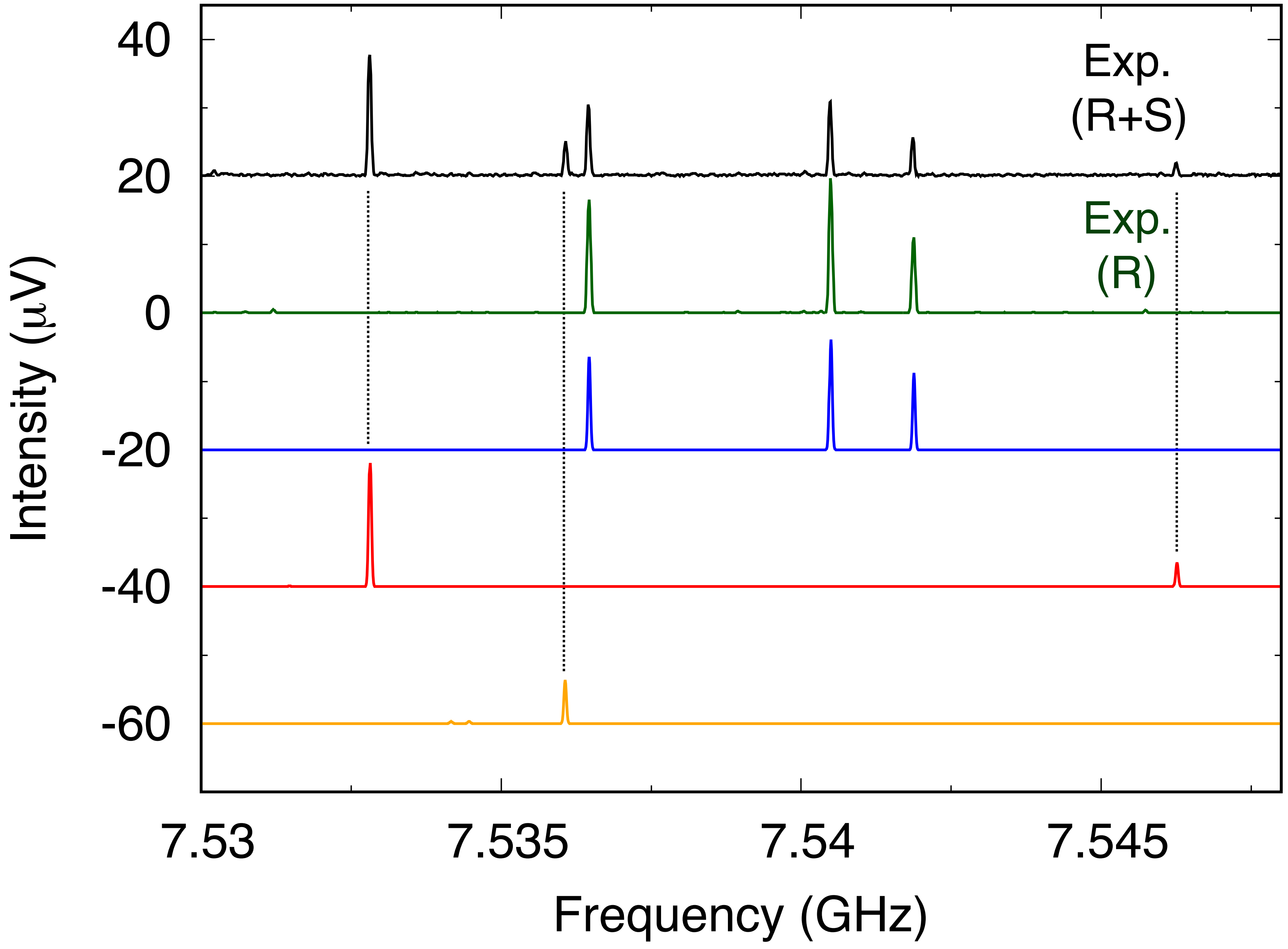

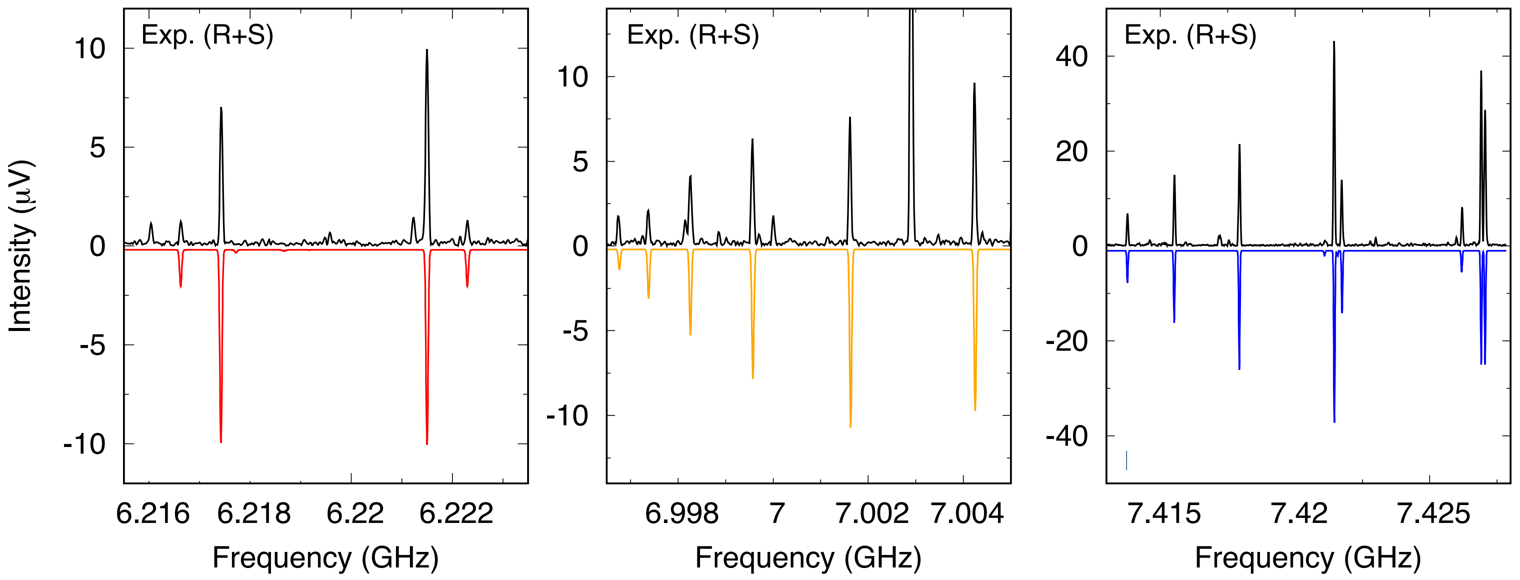

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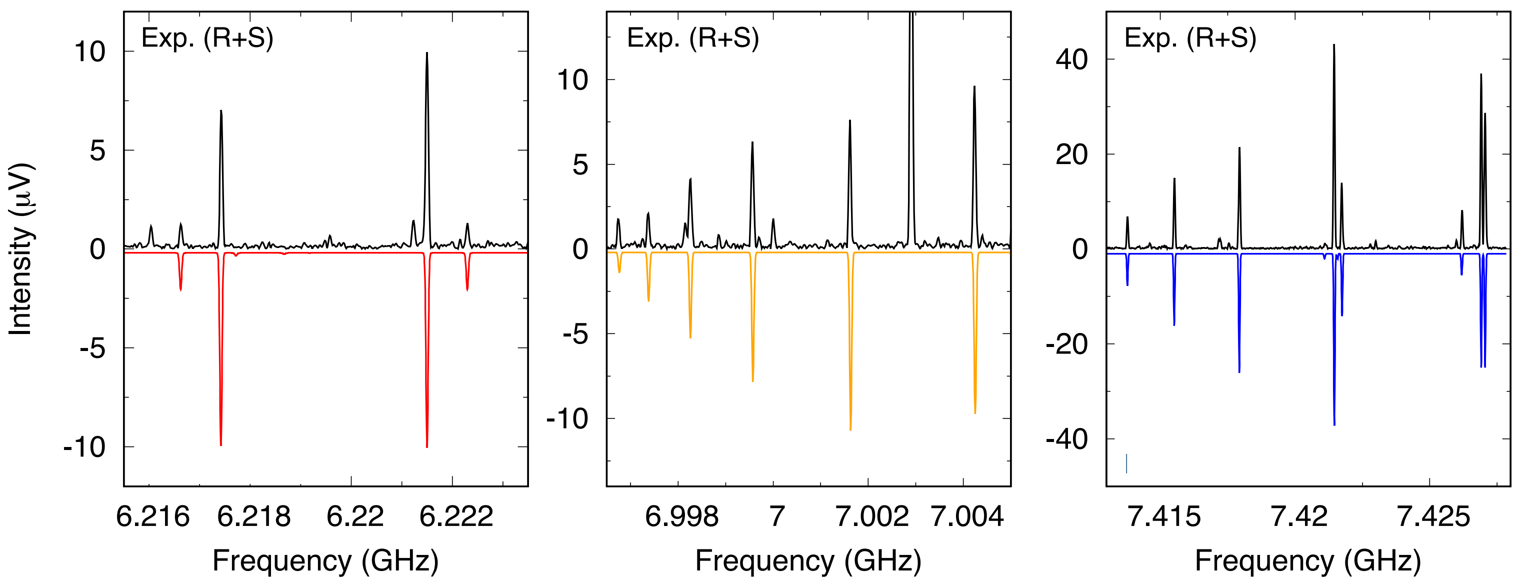

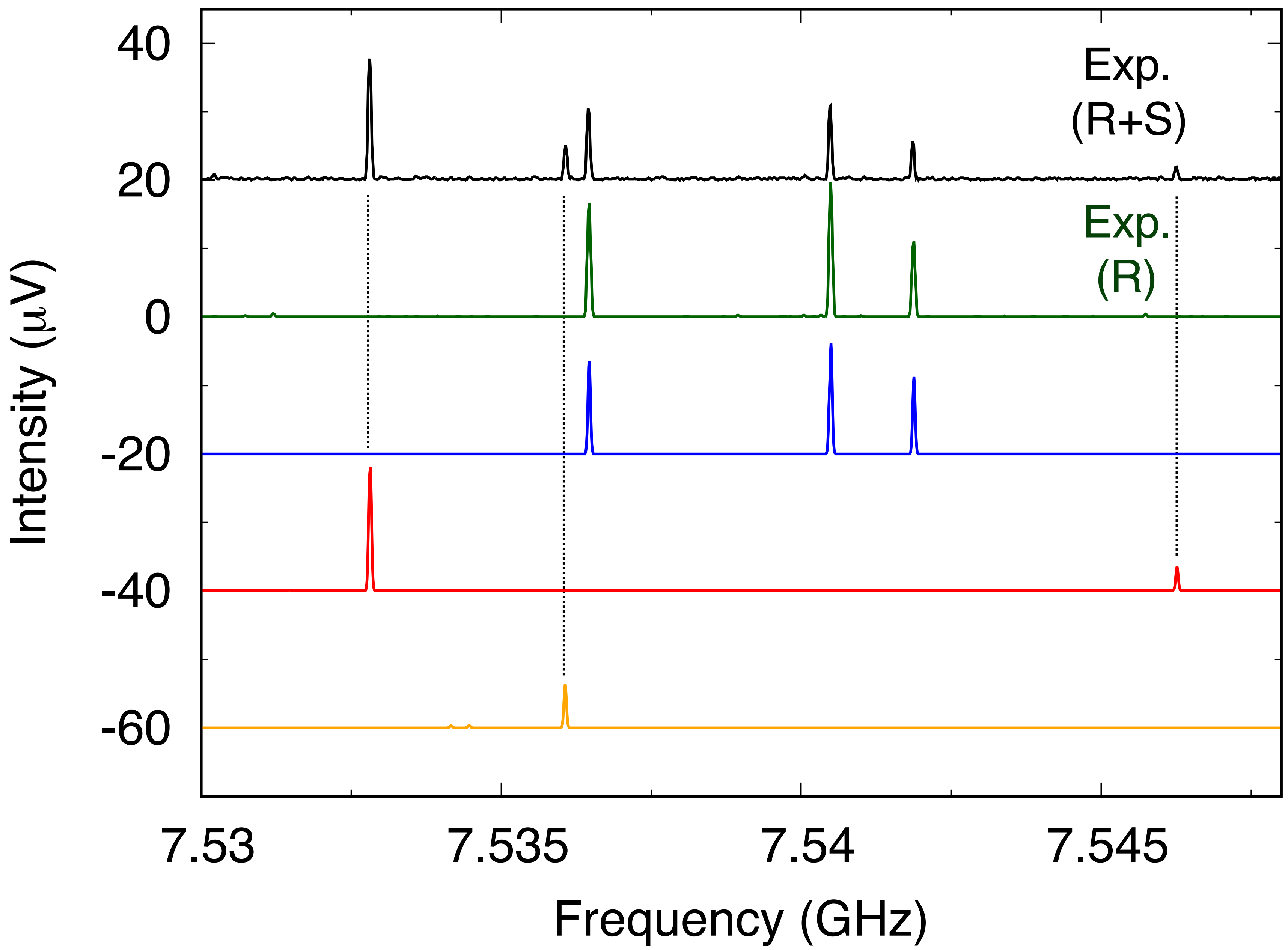

Homochiral

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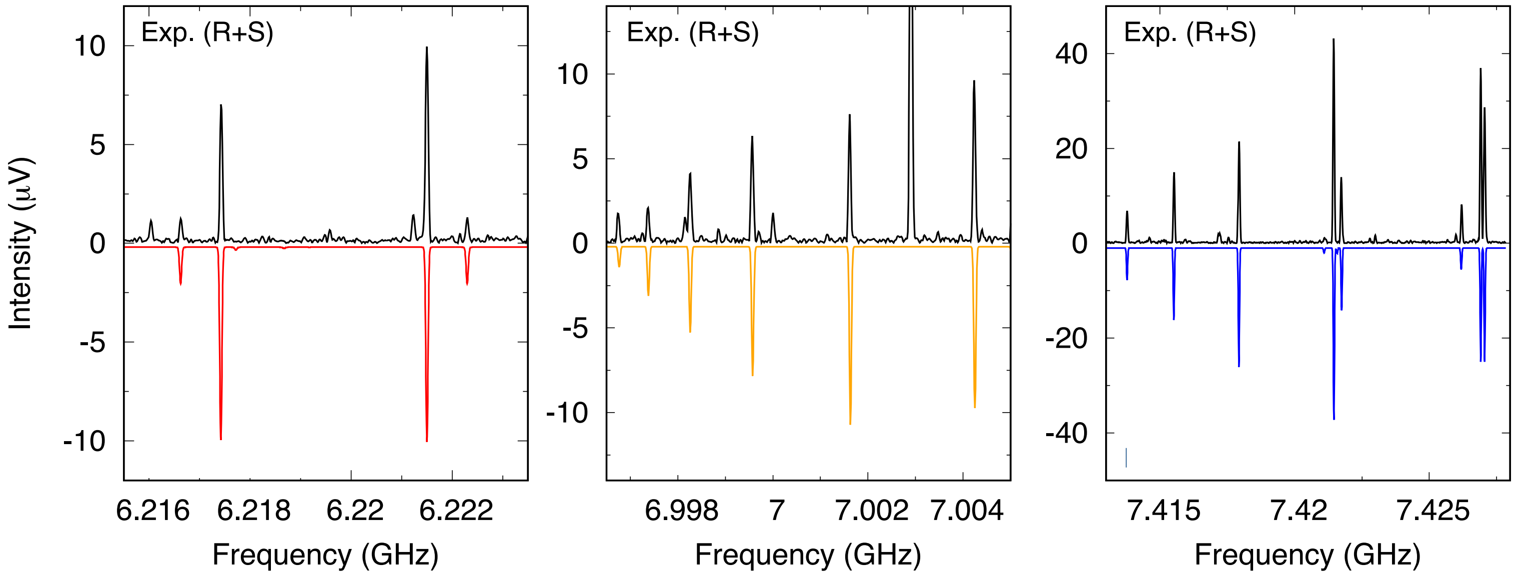

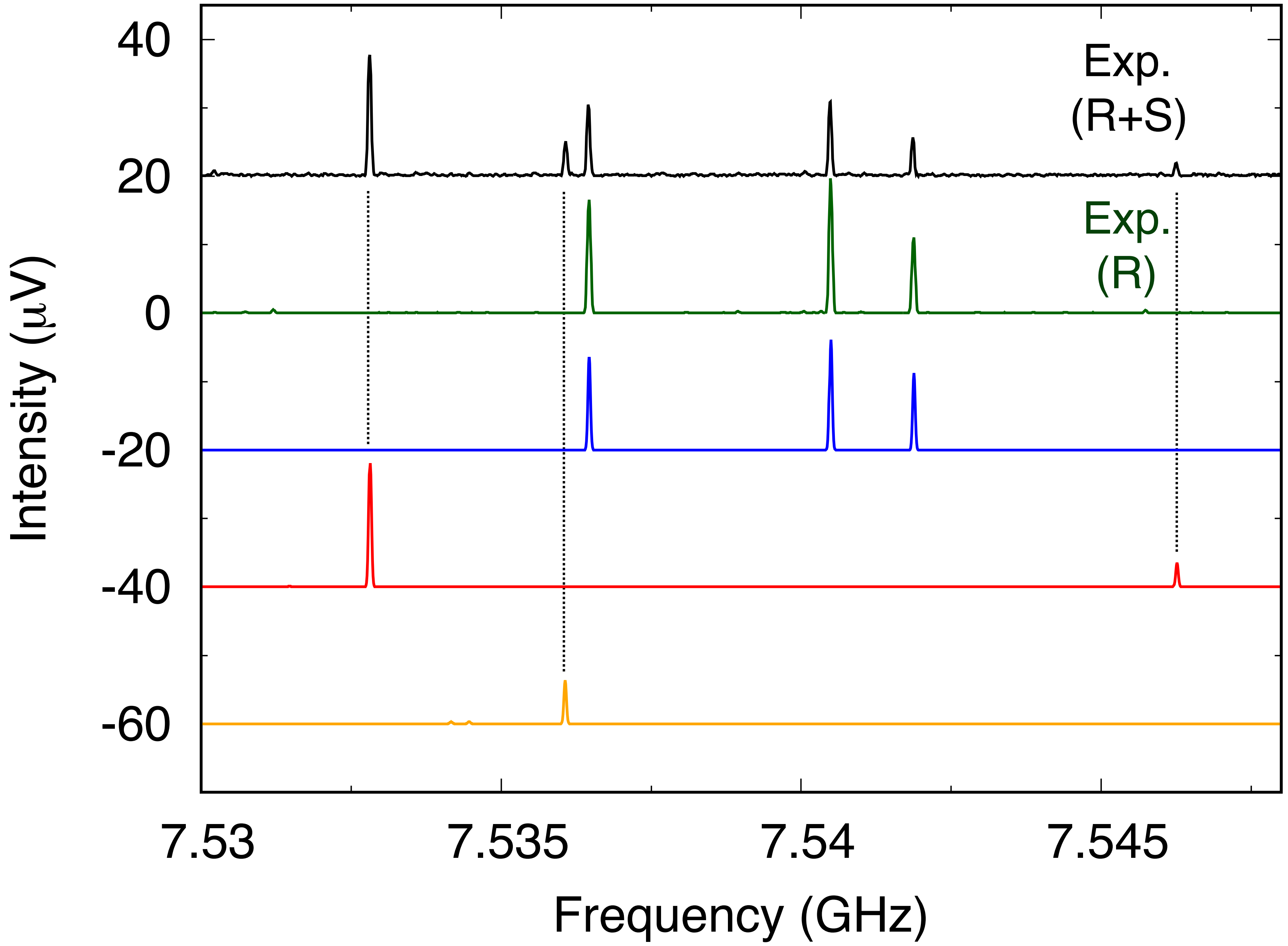

Homochiral

Heterochiral

Preferences of chiral aggregation.

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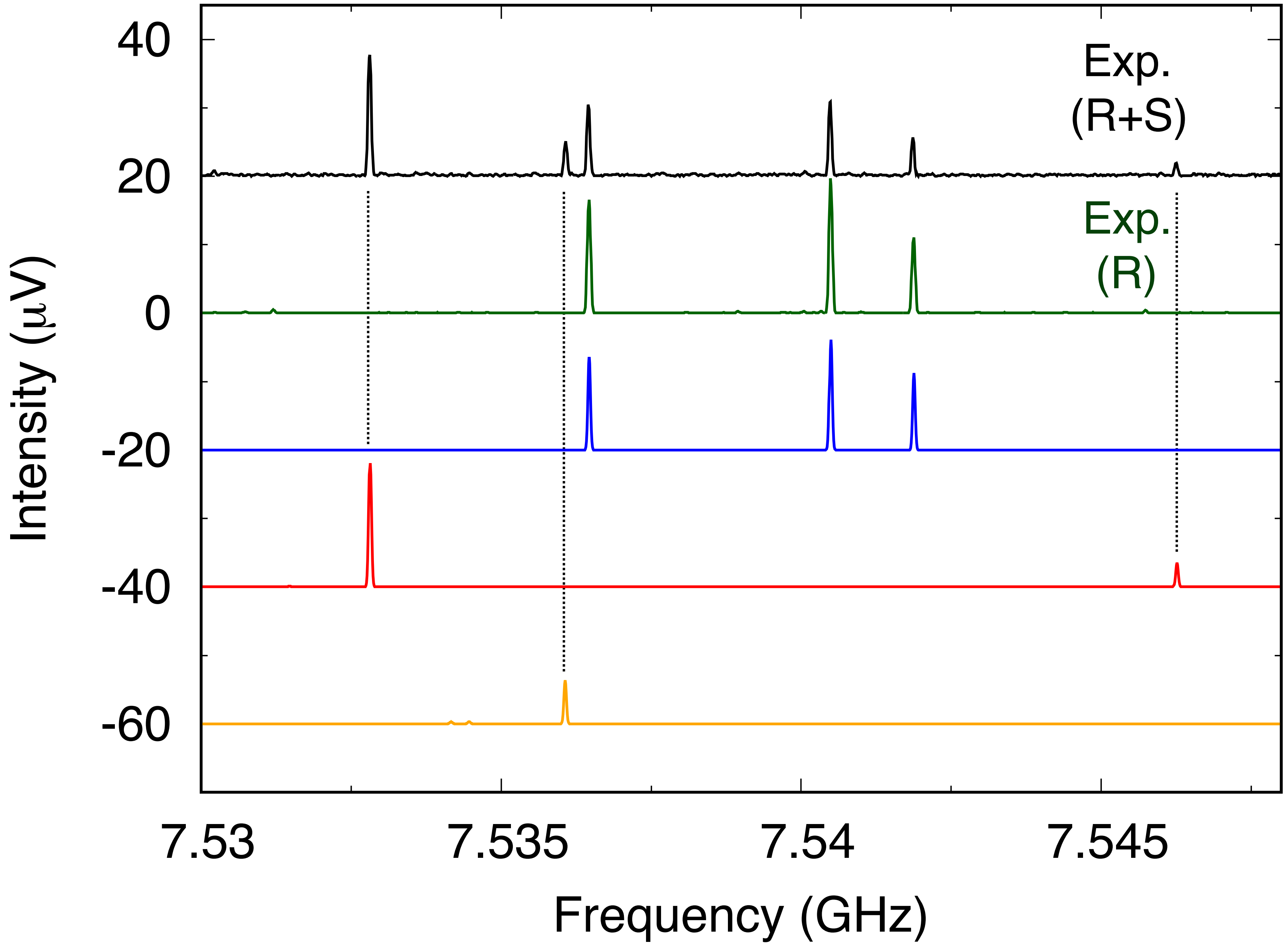
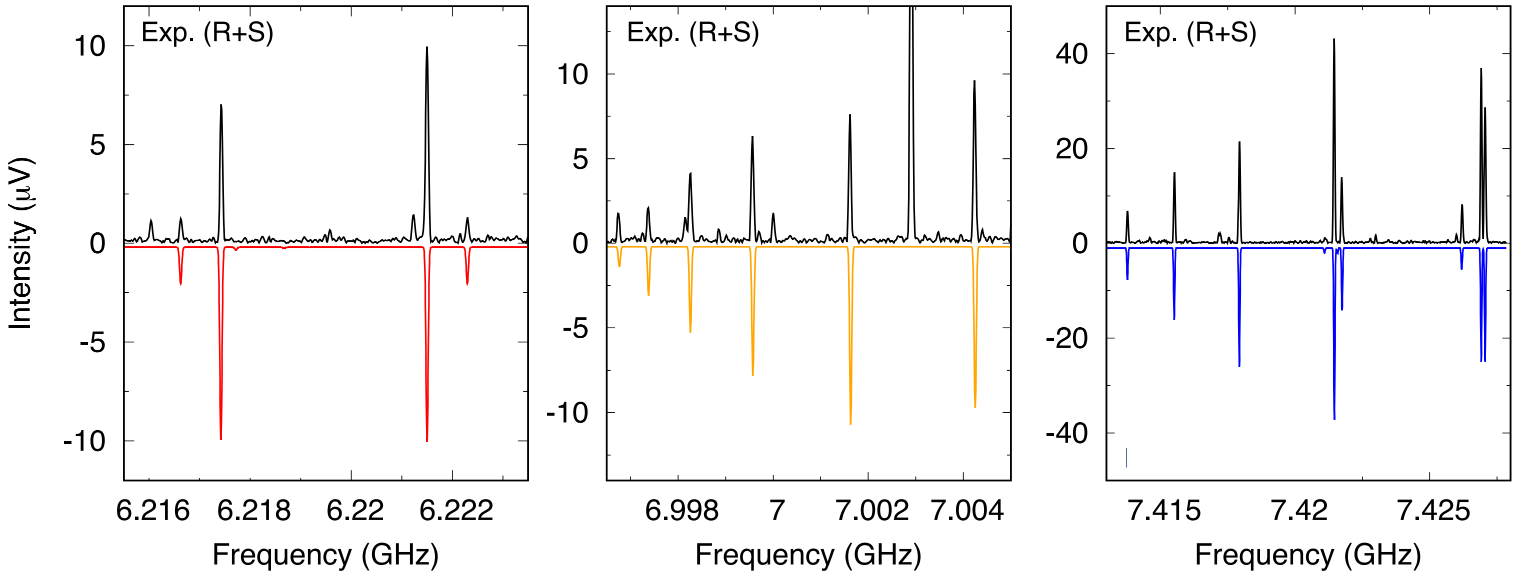


Homochiral

Heterochiral

Heterochiral



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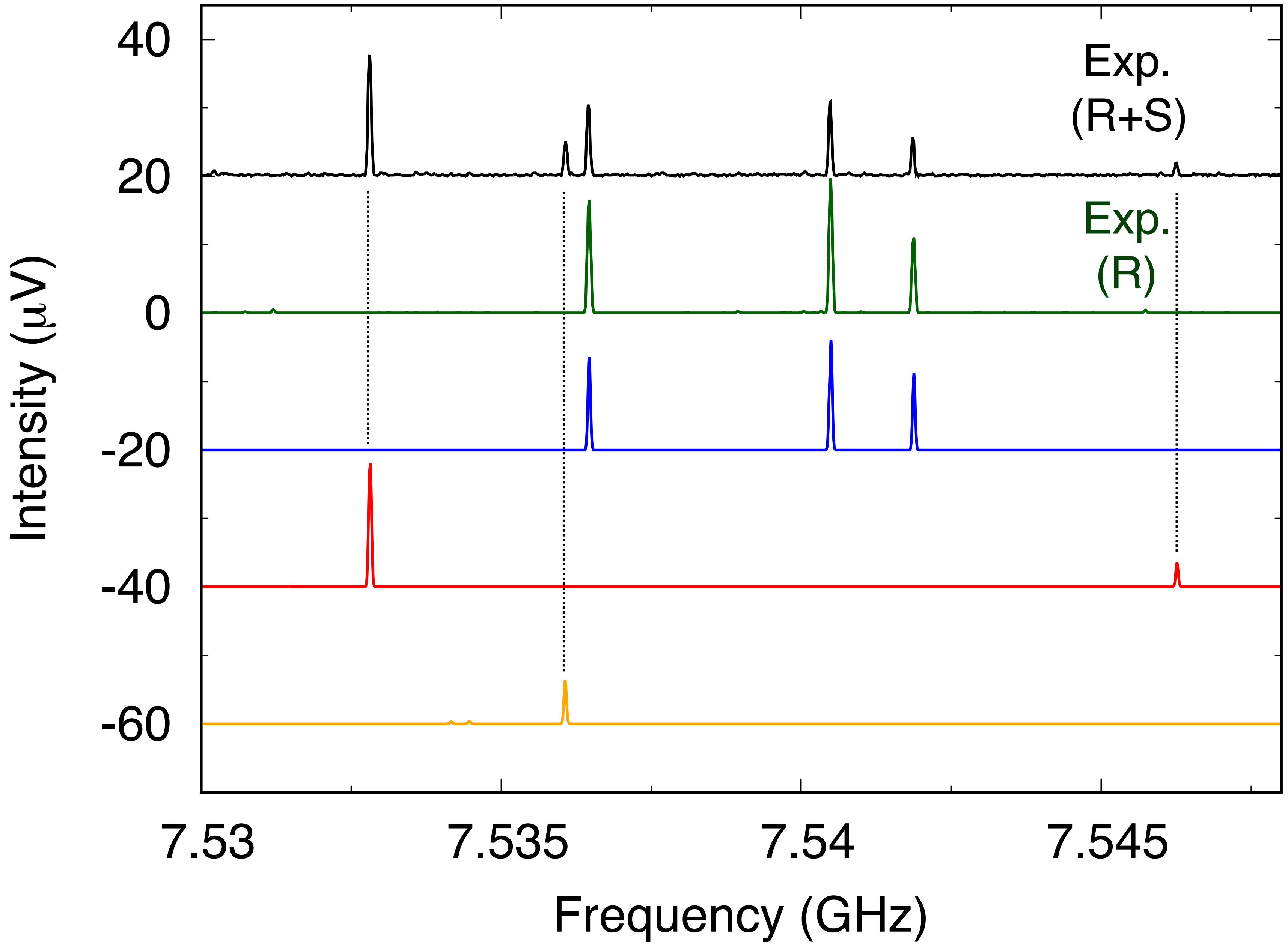
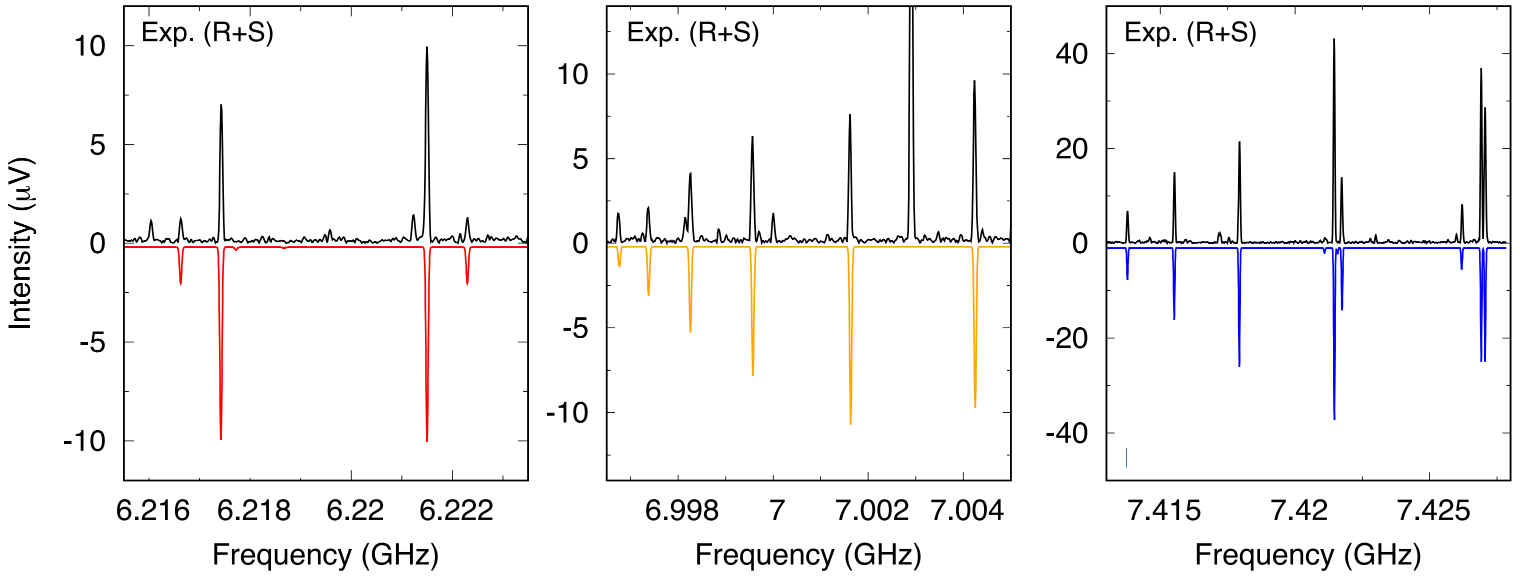


Homochiral

Heterochiral

Heterochiral



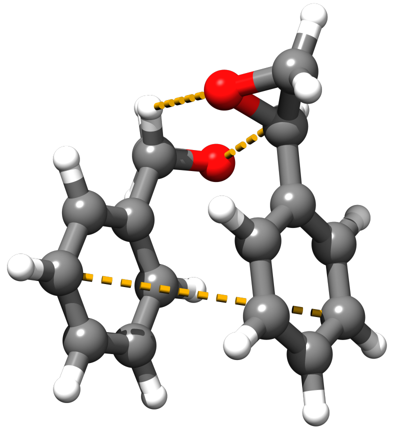
RS/SR **RS/SR** **RR/SS**

Quantum chemistry calculations.

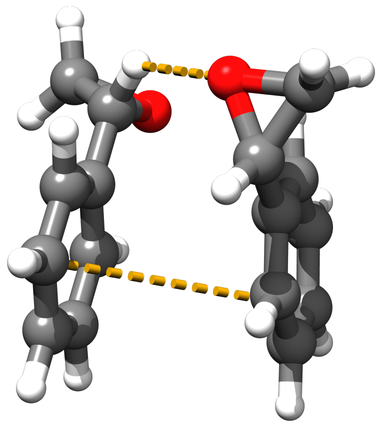
Assignment of homochiral and heterochiral dimer topologies

	ZPE/kJ·mol^{-1}	A/MHz	B/MHz	C/MHz	$\lvert\mu_a\rvert/D$	$\lvert\mu_b\rvert/D$	$\lvert\mu_c\rvert/D$
RR[0]	0.00	477.58	448.67	341.97	0.01	0.00	0.02
RS[1]	0.20	478.98	406.09	375.37	0.44	0.59	1.23
RR[2]	0.21	560.02	403.09	278.48	0.56	0.59	0.05
RR[3]	0.49	516.93	359.58	326.34	1.74	1.23	2.43
RR[4]	1.04	541.89	369.73	299.20	1.38	2.25	1.04
RS[5]	1.21	564.56	336.20	314.10	1.78	2.12	1.93

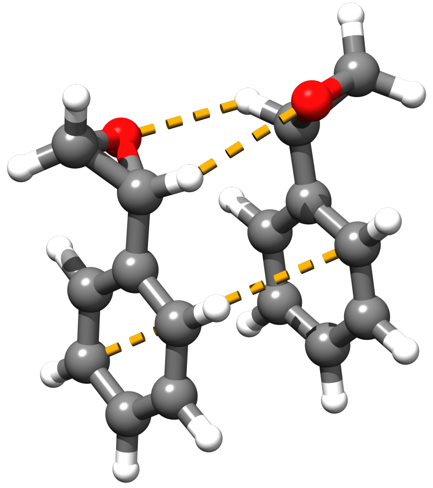
B3LYP-D3(BJ)/def2-pVTZ



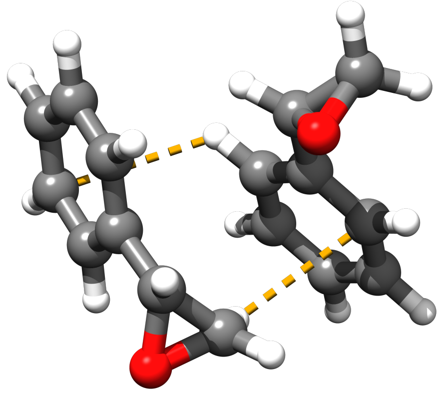
RR[0]



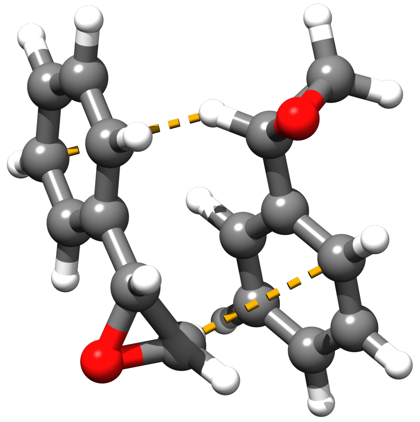
RS[1]



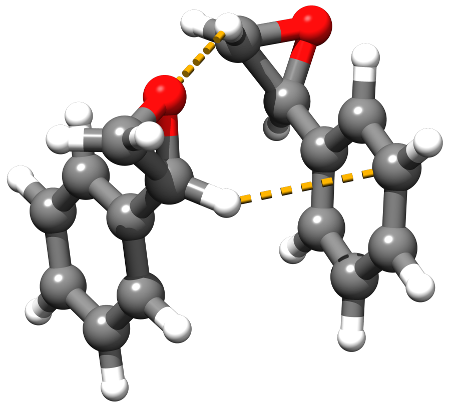
RR[2]



RR[3]



RR[4]



RS[5]

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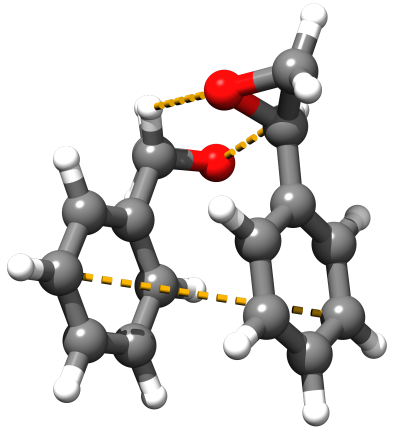
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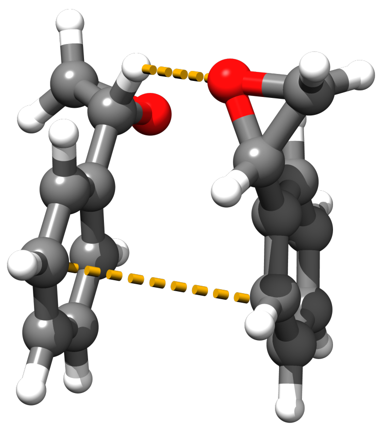
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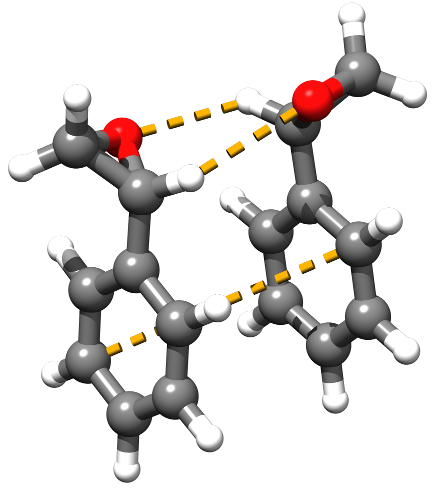
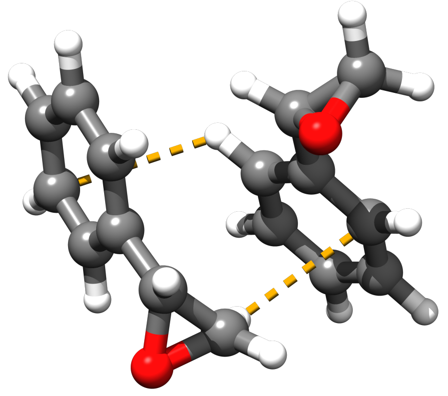
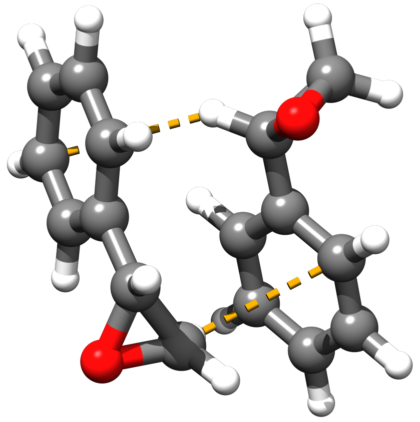
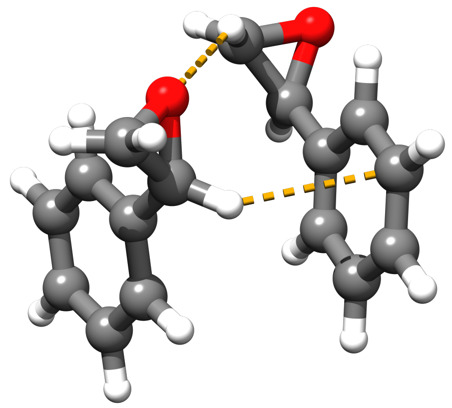

RR[2]


RR[3]


RR[4]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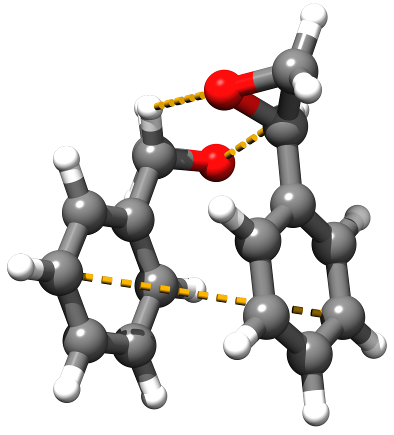
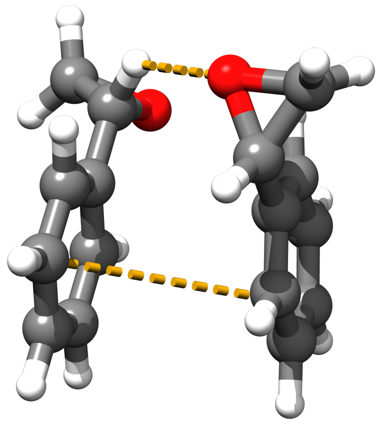
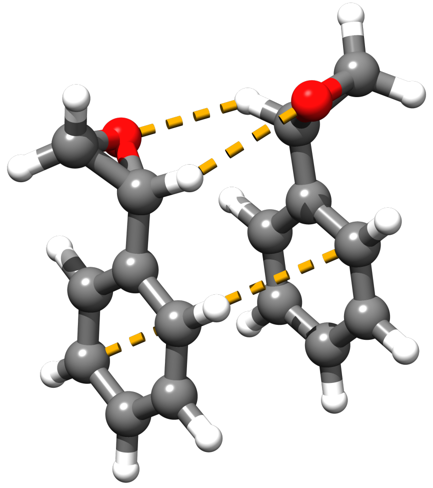


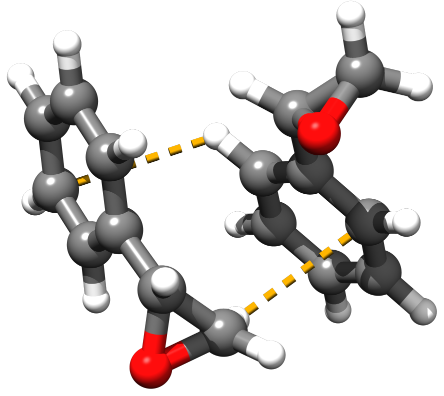
RR[0]



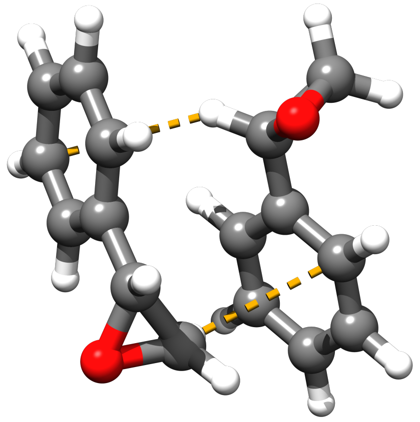
RS[1]



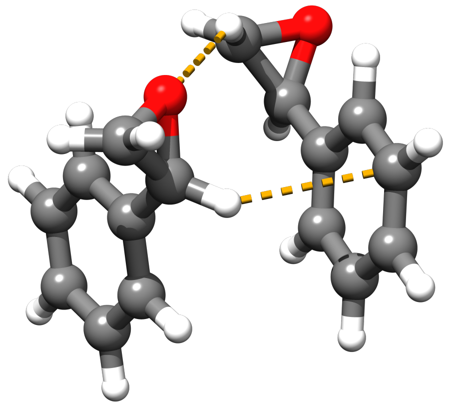
RR[2]



RR[3]



RR[4]



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near-oblate

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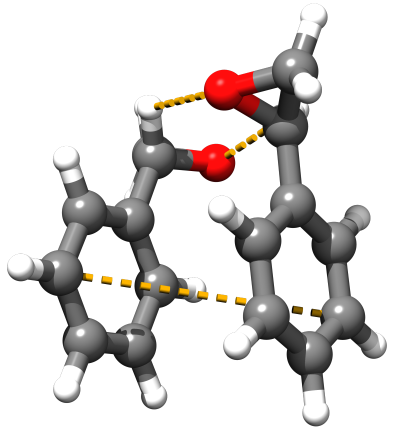
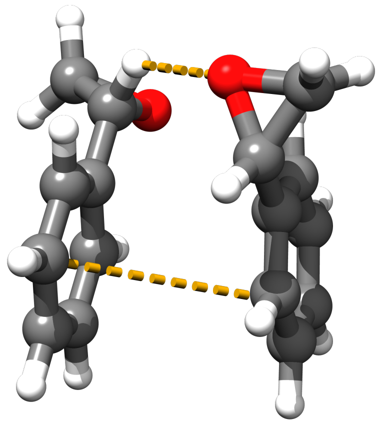
RR[0]	0.00	477.58	448.67	341.97	0.01	0.00	0.02
RS[1]	0.20	478.98	406.09	375.37	0.44	0.59	1.23
RR[2]	0.21	560.02	403.09	278.48	0.56	0.59	0.05
RR[3]	0.49	516.93	359.58	326.34	1.74	1.23	2.43
RR[4]	1.04	541.89	369.73	299.20	1.38	2.25	1.04
RS[5]	1.21	564.56	336.20	314.10	1.78	2.12	1.93

near-prolate

B3LYP-D3(BJ)/def2-pVTZ



RR[0]



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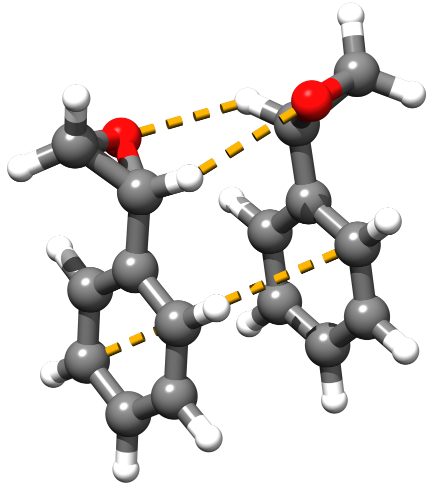
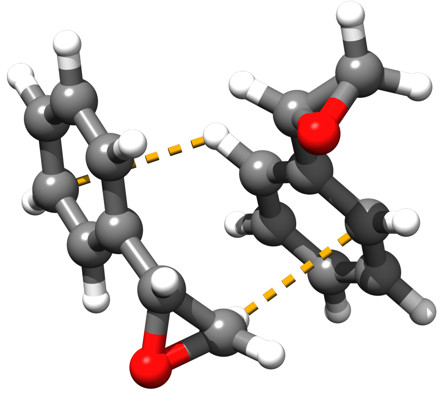
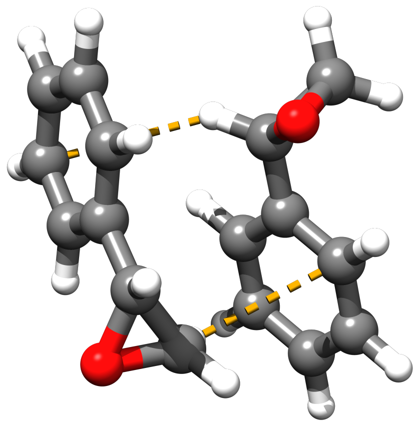


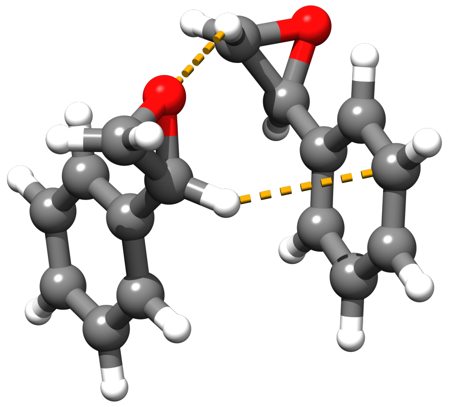
RR[2]



RR[3]



RR[4]



RS[5]

Quantum chemistry calculations.

Assignment of homochiral and heterochiral dimer topologies

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B3LYP-D3(BJ)/def2-pVTZ

Experimentally determined rotational constants

A **565.13225(13) MHz**	**A** **519.837930(80) MHz**	**A** **476.41136(25) MHz**
B **327.768166(84) MHz**	**B** **350.271868(52) MHz**	**B** **399.70557(17) MHz**
C **307.883749(90) MHz**	**C** **322.618173(56) MHz**	**C** **371.57733(16) MHz**

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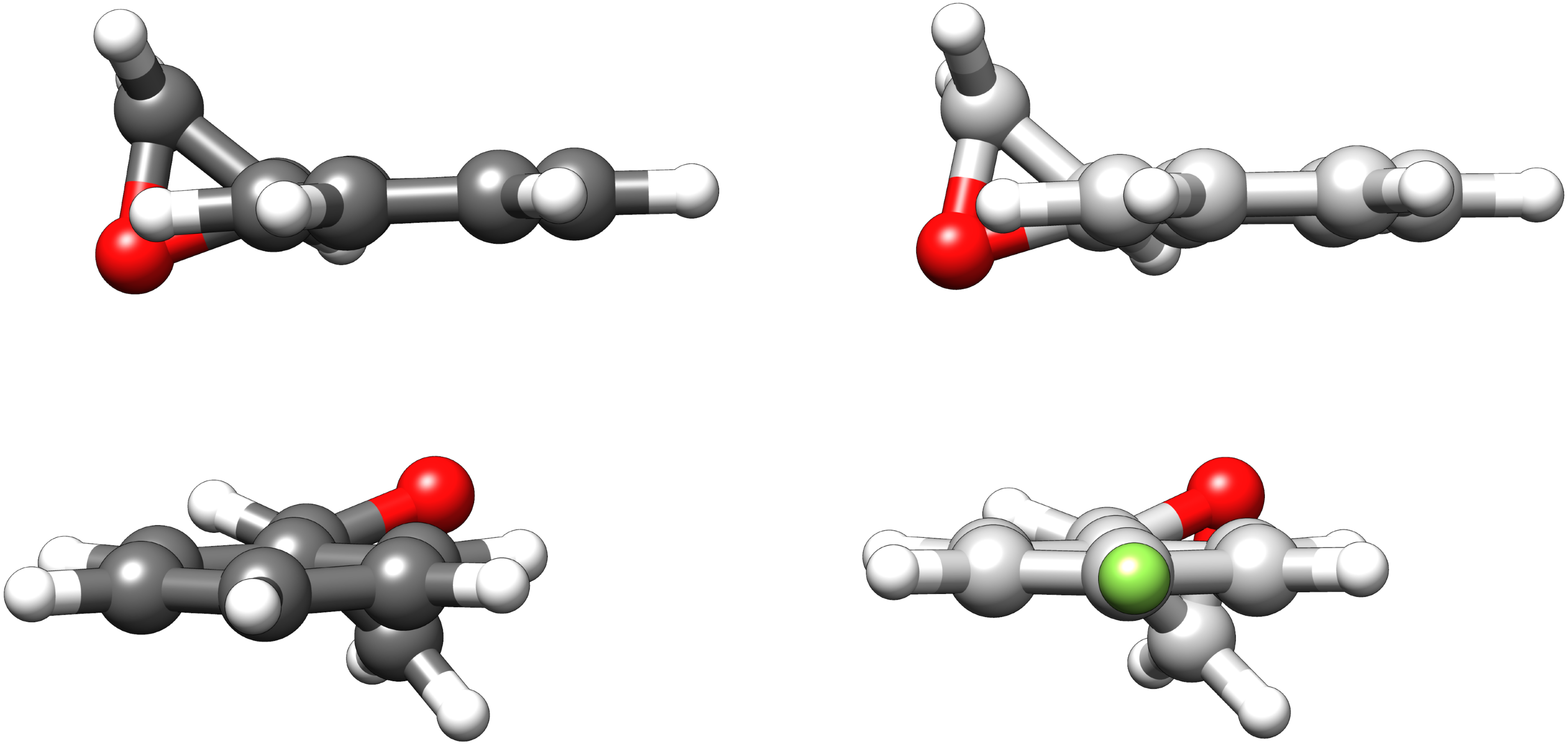
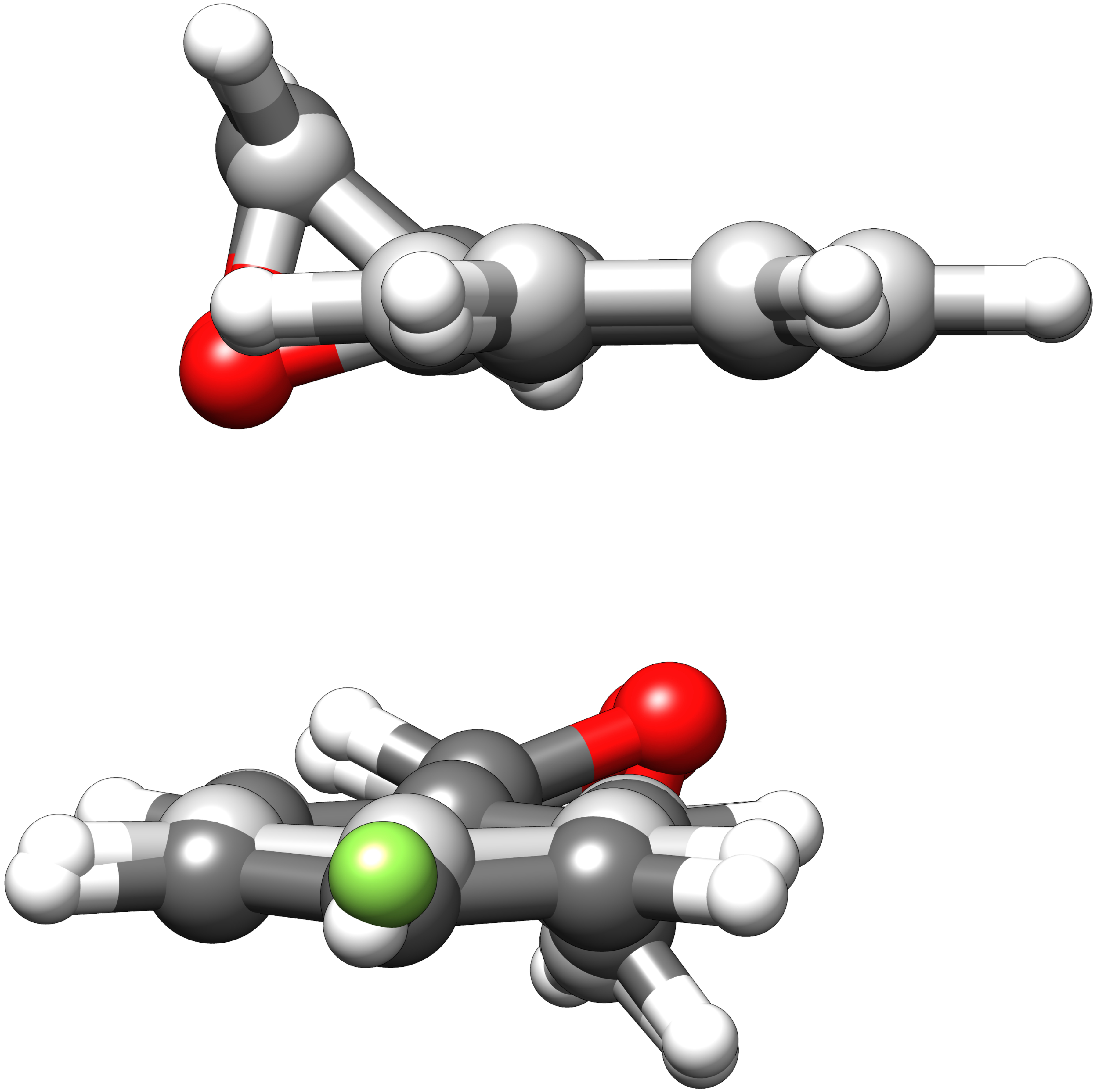
The non-polar global minimum RR[0]

Using fluorinated styrene oxide - side views



The non-polar global minimum RR[0]

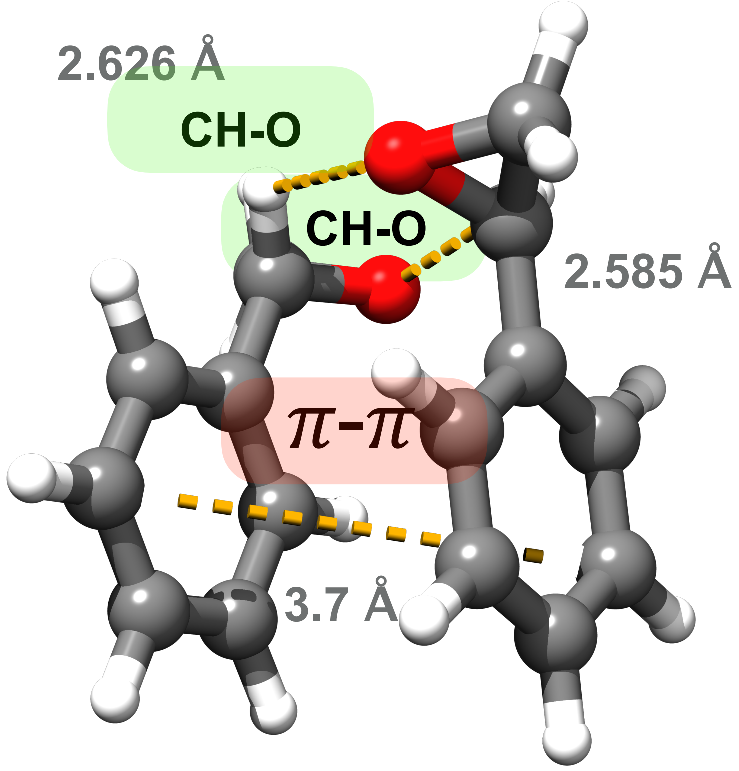
Using fluorinated styrene oxide - overlays



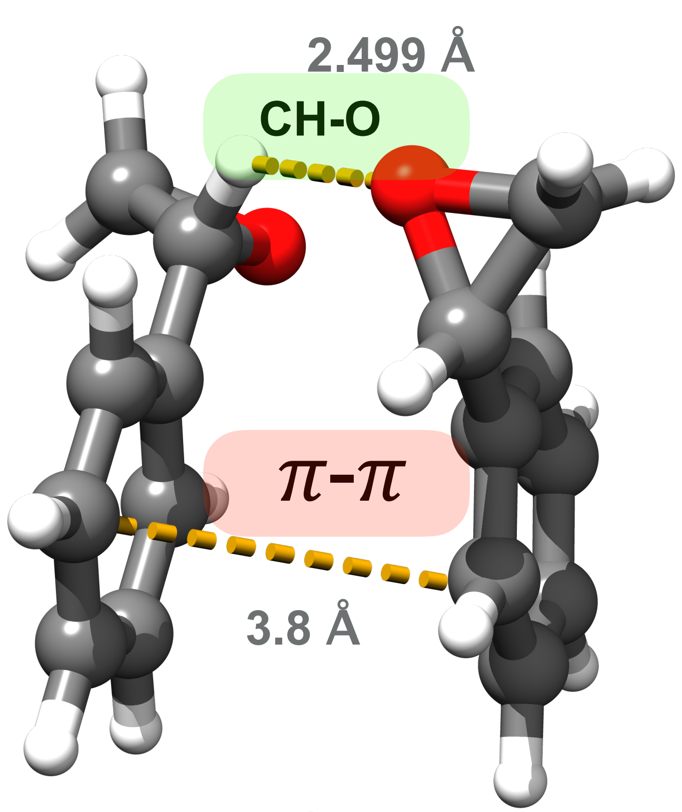
Topologies.

Homochiral vs Heterochiral

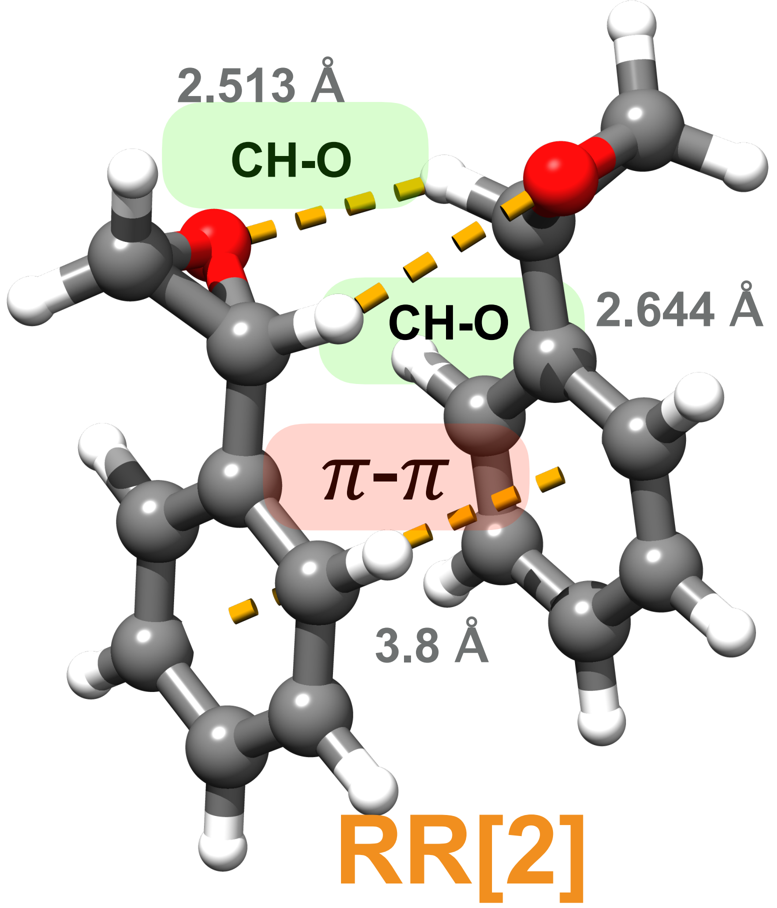
- **3 non-covalent contacts**
- **benzene arrangement similar to parallel-displaced benzene dimer**



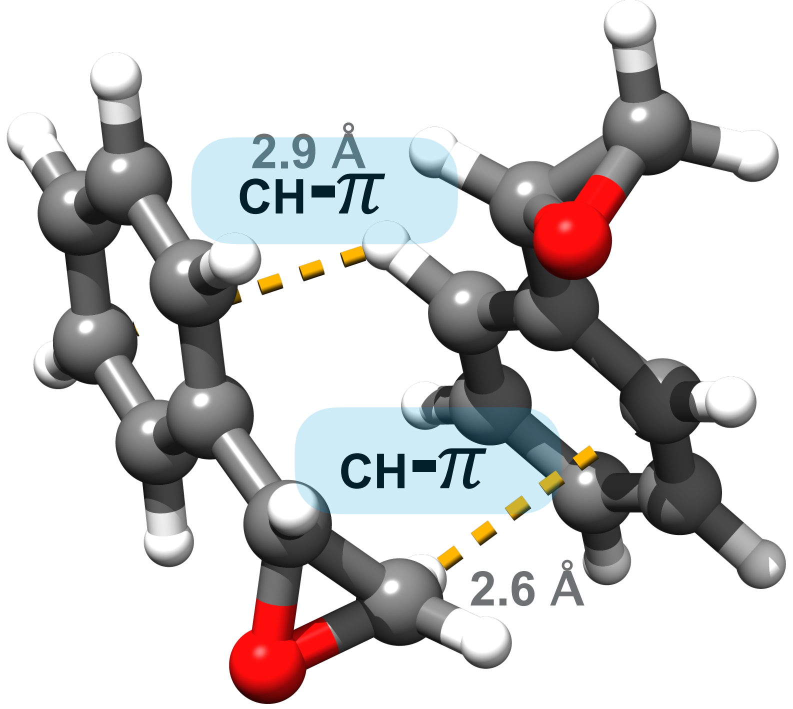
RR[0] (non polar)



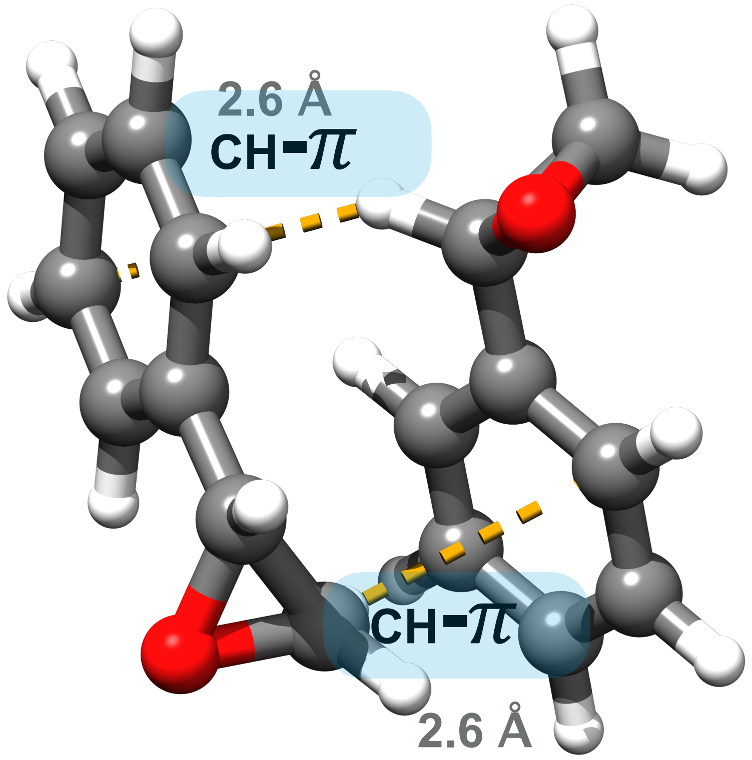
RS[1]



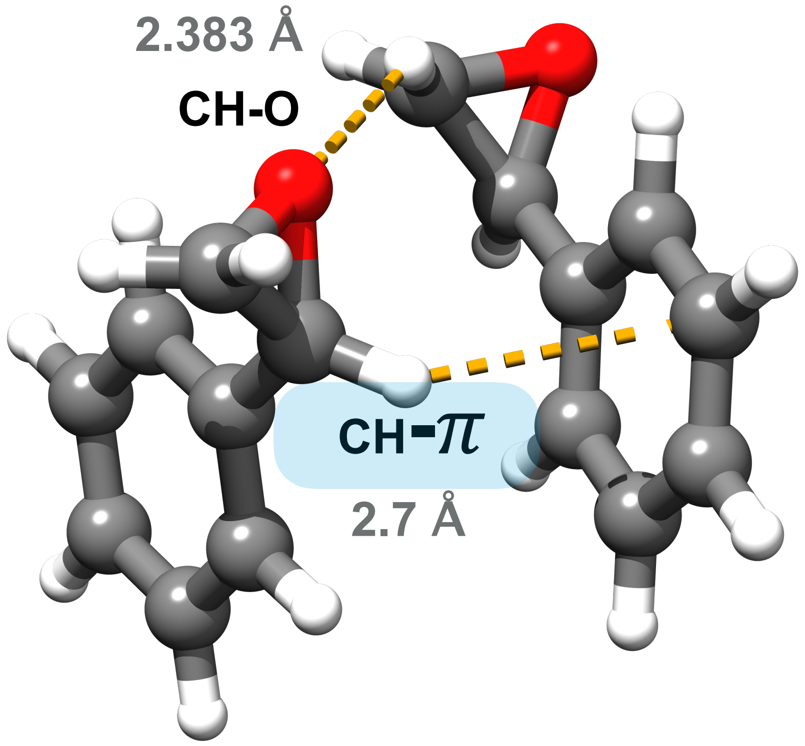
RR[2]



RR[3]



RR[4]



RS[5]

- **one oxirane group points away**

Intermolecular interactions.

What are the binding forces at play?

SAPT(0)/jun-cc-pVDZ

	ΔE_{elec}	ΔE_{ind}	ΔE_{disp}	ΔE_{exch}	ΔE_{tot}
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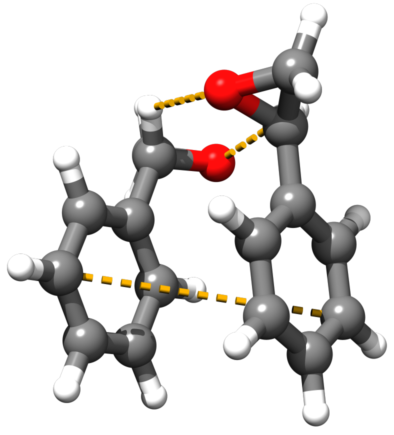
kJ·mol^{-1}



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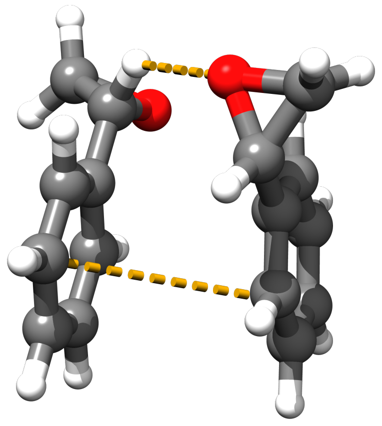

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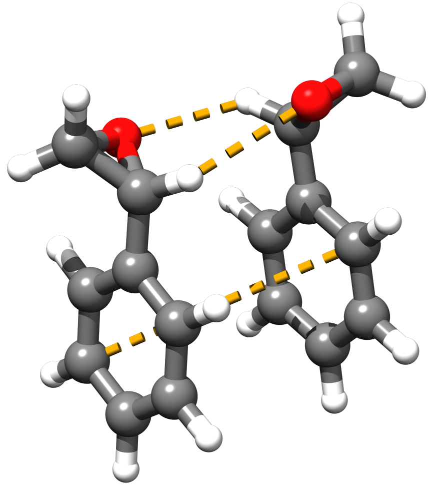
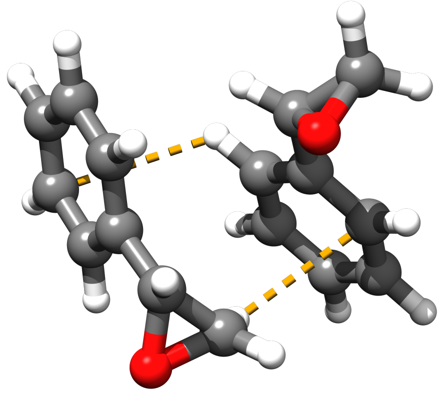
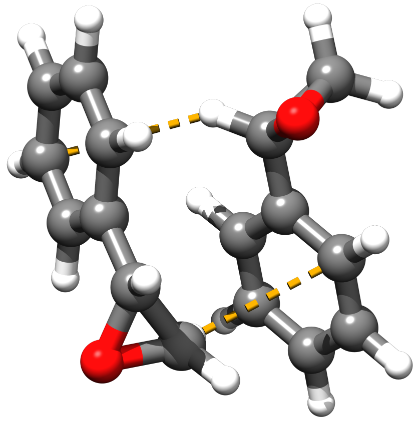


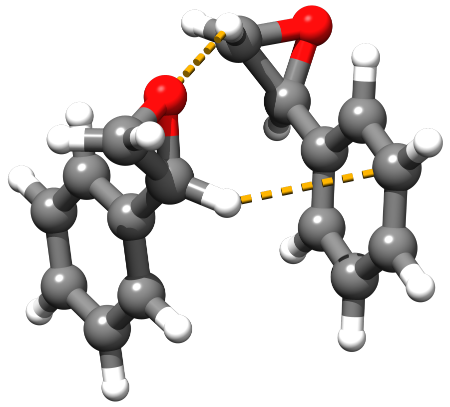
RR[2]



RR[3]



RR[4]



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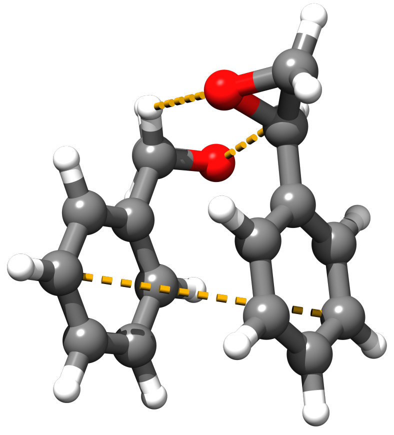
$\mathrm{kJ \cdot mol^{-1}}$



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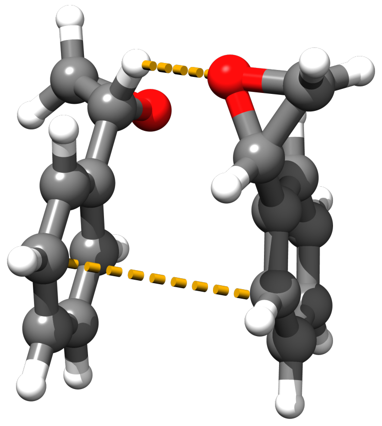

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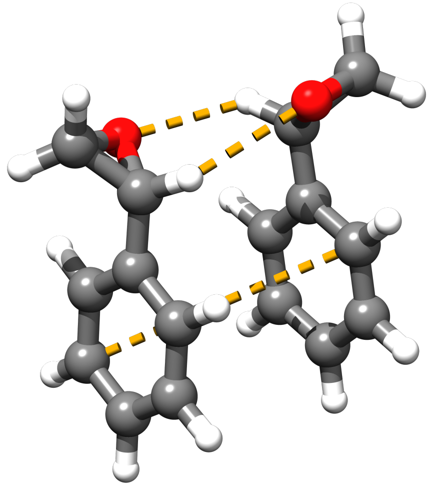

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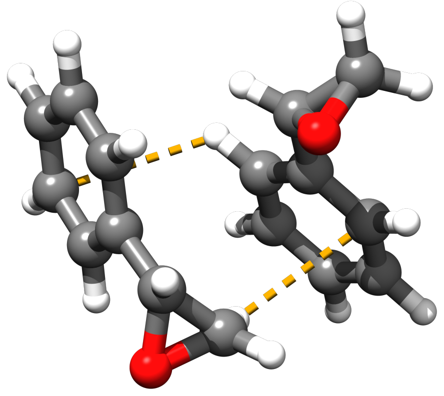

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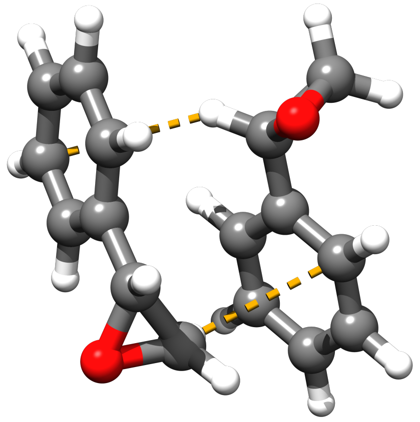

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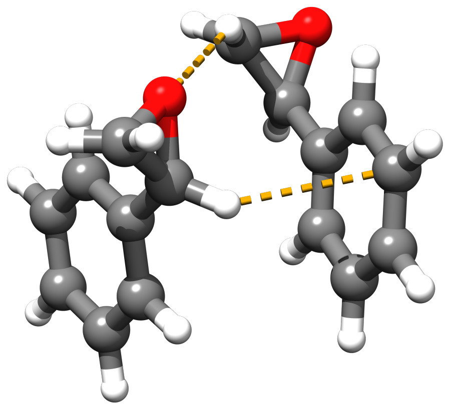
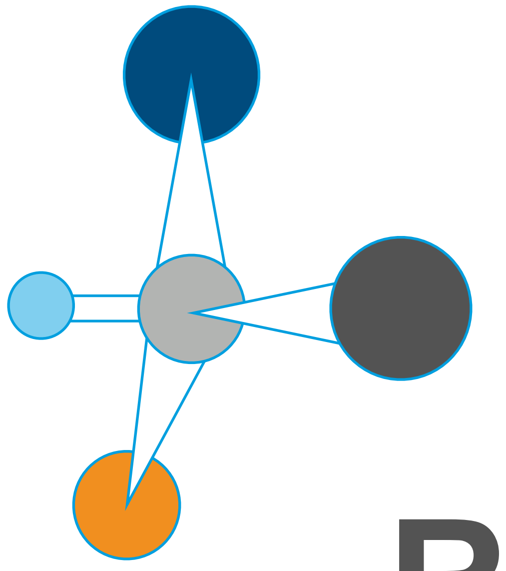
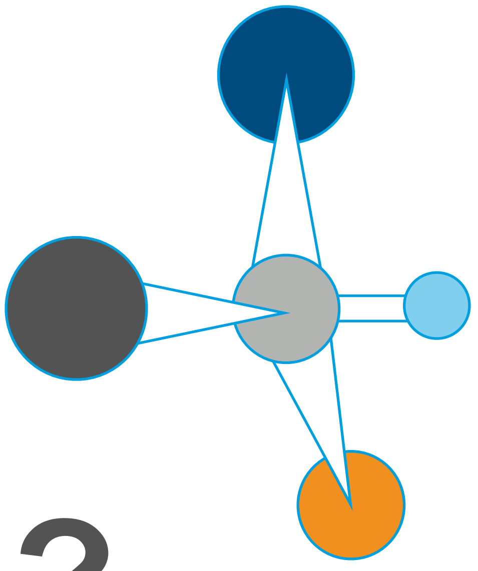


RS[5]

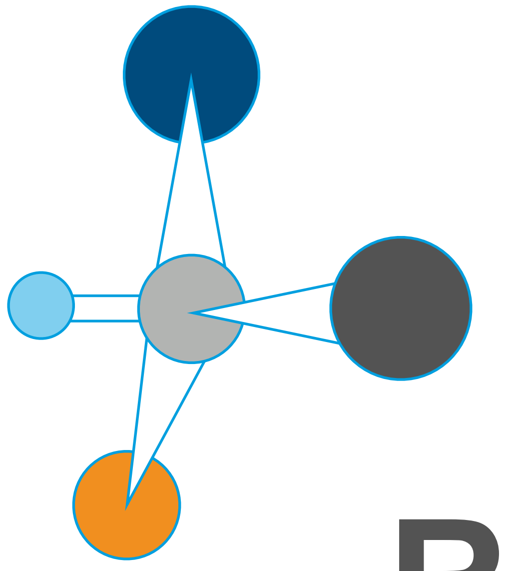
Absolute configuration of a chiral molecule.

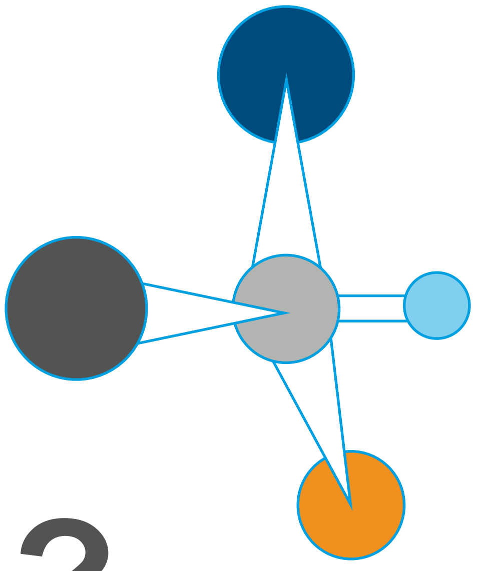




R or S?

Absolute configuration of a chiral molecule.





R or S?

“Pair me, and I will tell you who I am.”

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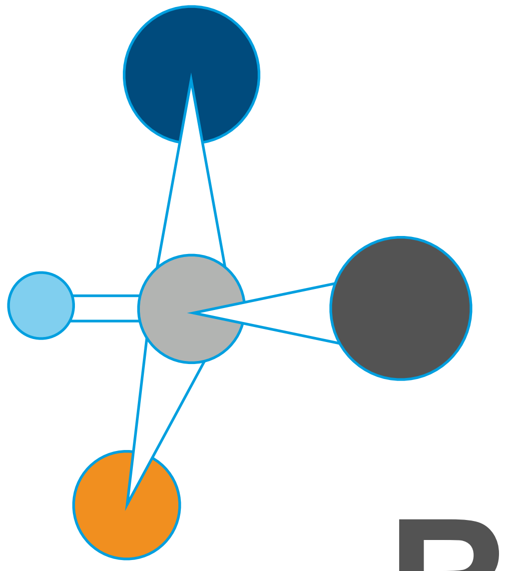

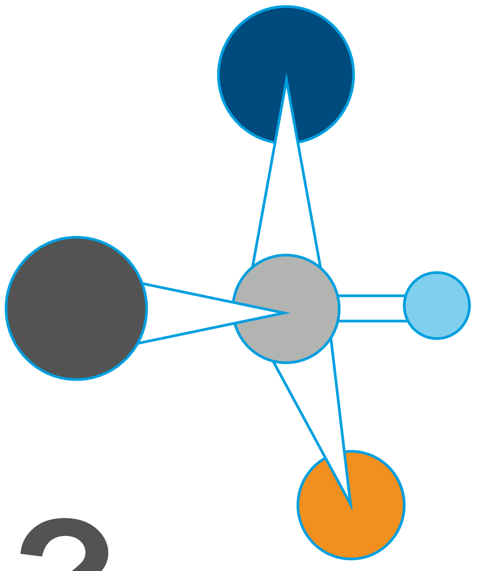

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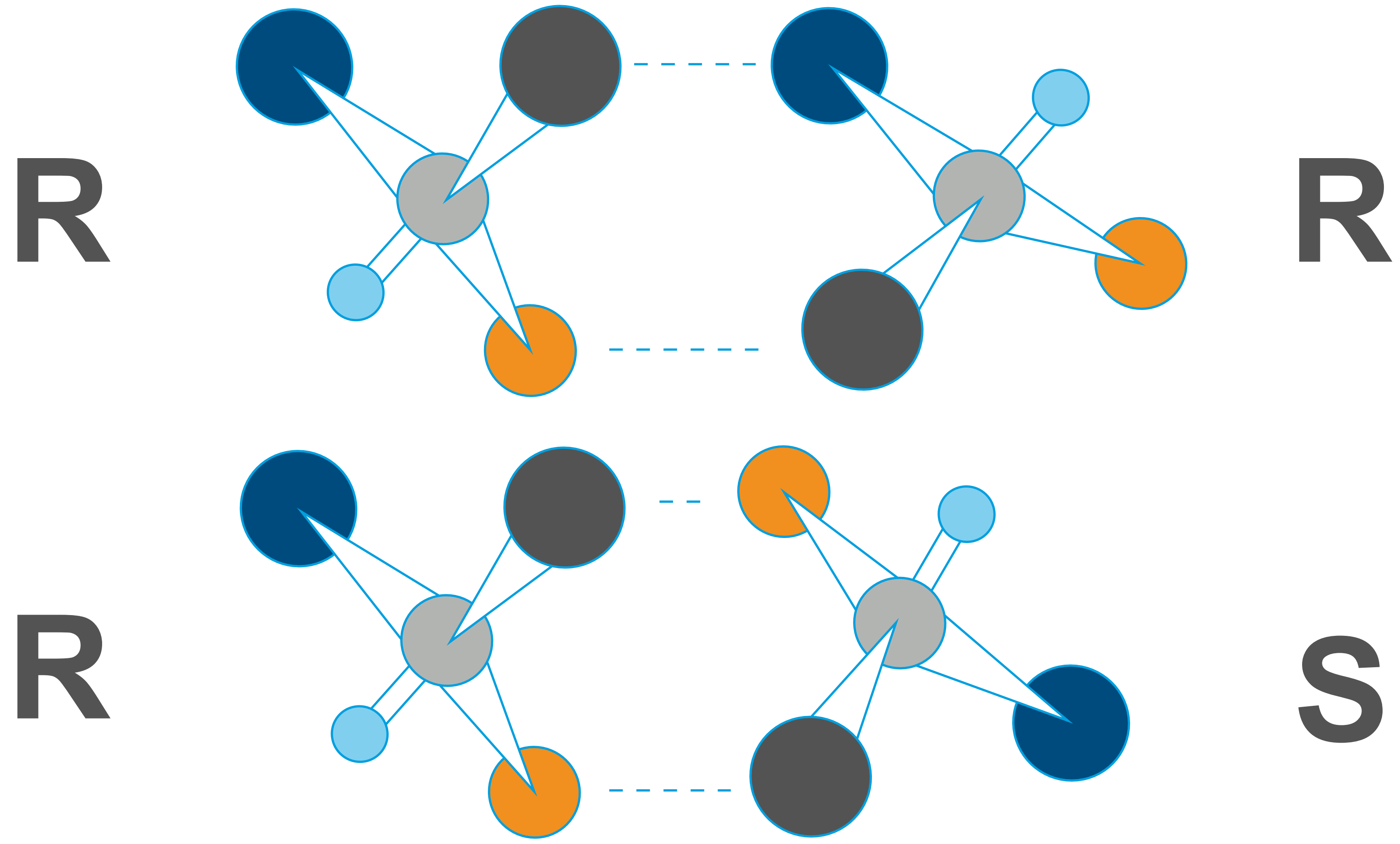
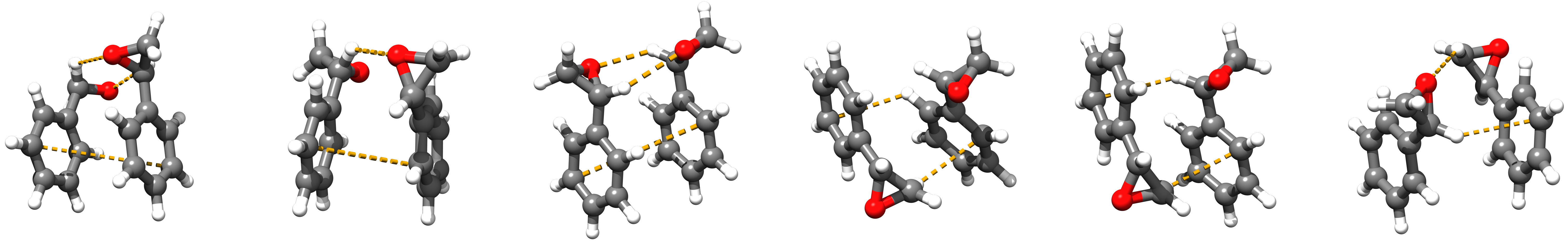


Take home messages.

Conclusions

- **Styrene oxide dimer:**
  - 3 non-covalent interaction contacts
  - two qualitatively different classes of molecular complexes, which differ by the arrangement of the oxirane ring and the amount of dispersion interaction

- Clustering chiral molecules transforms **enantiomers** into **diastereomers**, greatly simplifying the **absolute configuration** problem.



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SPP 1807
Dispersion

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ELCH

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FCI
FONDS DER CHEMISCHEN INDUSTRIE

Alexander von Humboldt
Stiftung/Foundation

SPP 1807
Dispersion

erc
European Research Council

CUI THE HAMBURG CENTRE FOR ULTRAFAST IMAGING

The group

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