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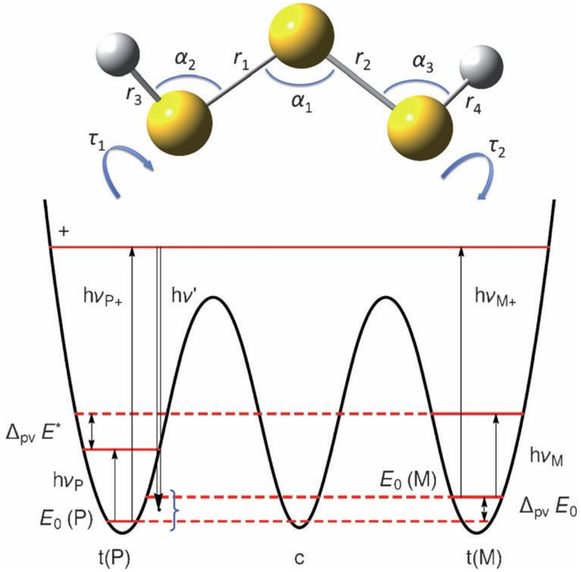

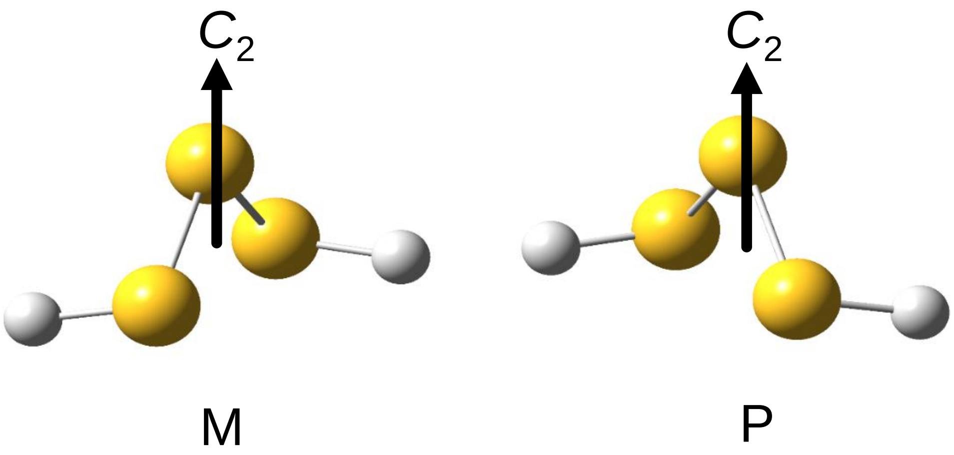

HIGH RESOLUTION FTIR SPECTROSCOPY OF TRISULFANE (HSSSH): A CANDIDATE FOR DETECTING PARITY VIOLATION IN CHIRAL MOLECULES

S. Albert,I. Bolotova,Z. Chen,C. Fábri, M. Quack,G. Seyfang and D. Zindel

(*Phys. Chem. Chem. Phys.,* 2017, 19, 11738-11743)

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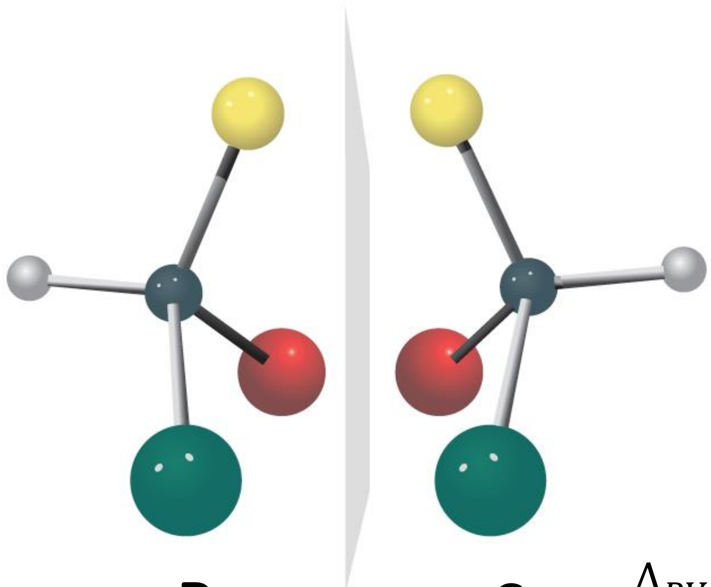
Energy difference in enantiomers of a chiral molecule

Traditional theory:

van‘t Hoff 1887

$R \rightleftarrows S \quad \Delta_R H_0^\ominus = 0$

exactly by symmetry



Today:

electroweak parity violation

$\Delta_{PV} H_0^\ominus = \Delta_{PV} E_0 \times N_A$

$\cong 10^{-(11 \pm 2)}$ J/mol

$\Delta_{PV} E_0 \cong 100 aeV$
$\cong (hc) \cdot 10^{-12}\ cm^{-1} \cong h \cdot 25\ m\mathrm{Hz}$

Example : CHBrClF

M. Quack and J. Stohner, *Phys. Rev. Lett.* **84**, 3807-3810 (2000)

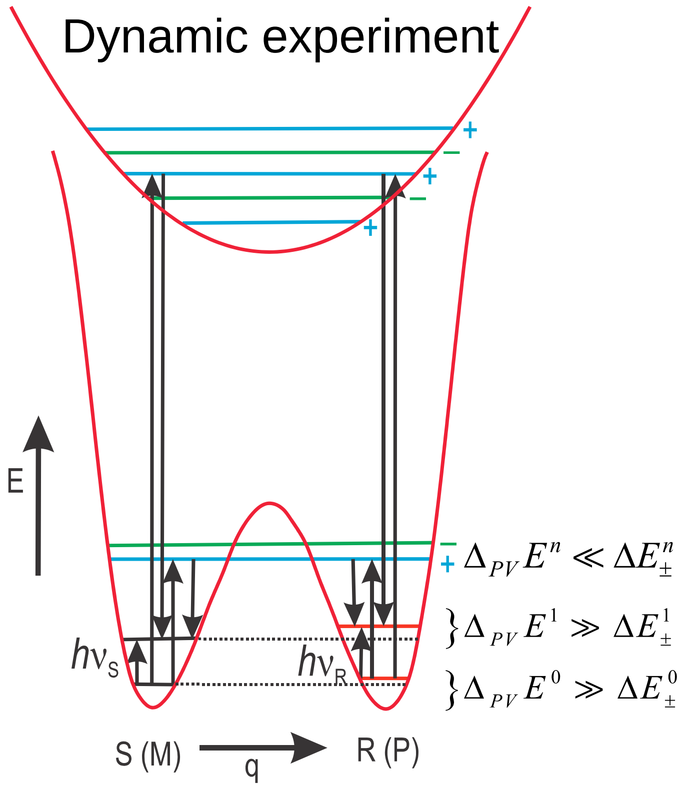
Schemes to measure molecular parity violation

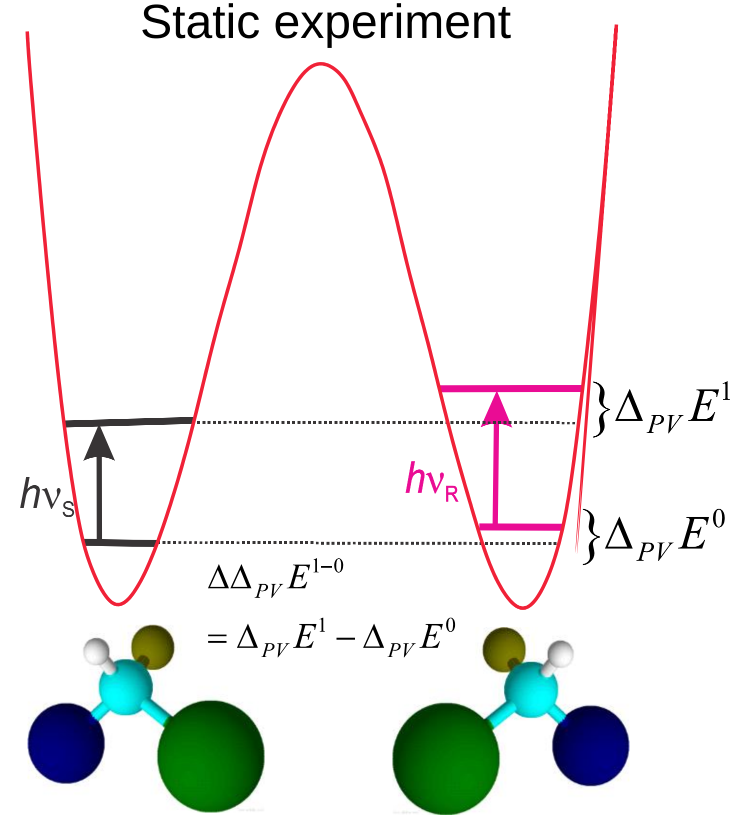
V. Letokhov, *Phys. Lett. A* 53 (4), 275 (1975) (CHFClBr)

A. Bauder, A.Beil, D.Luckhaus, F. Müller and M. Quack, *J. Chem.Phys*. 106, 7558 (1997)

C. Daussy, T. Marrel, A. Amy-Klein, C. Nguyen, C. Borde, and C. Chardonnet, *Phys. Rev. Lett*. 83, 1554 (1999)

M. Quack, *Chem. Phys. Lett*. 132, 147 (1986);
M. Quack, *Angew.Chem.Int.Ed.* 28,571 (1989)



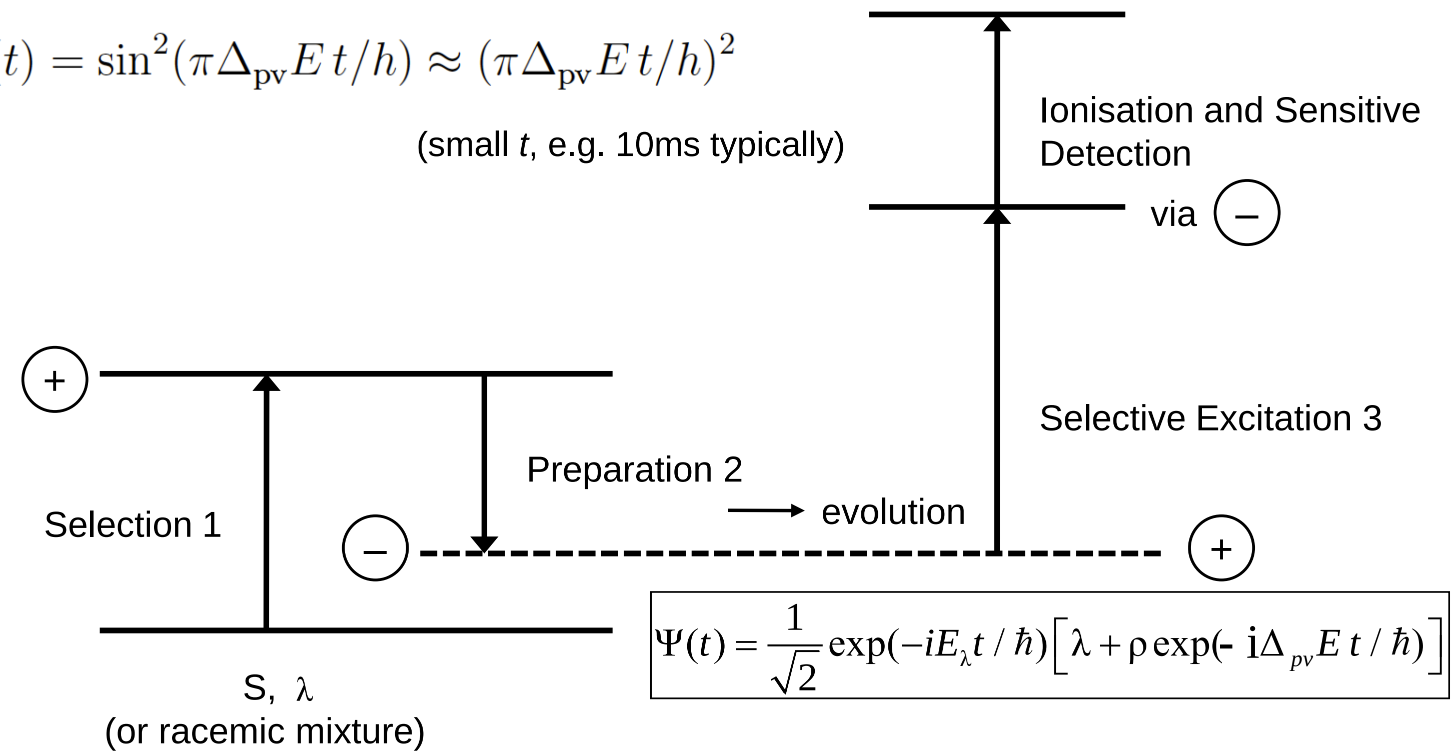


Review: M. Quack, in "Handbook of High-Resolution Spectroscopy", Vol.1, Chapter 18, 659–722, M. Quack and F. Merkt, Eds., Wiley, Chichester,2011.

Current experimental scheme to detect parity violation: Selection-Preparation-Evolution-Detection

$$p(t) = \sin^2(\pi \Delta_{\rm pv} E\, t/h) \approx (\pi \Delta_{\rm pv} E\, t/h)^2$$

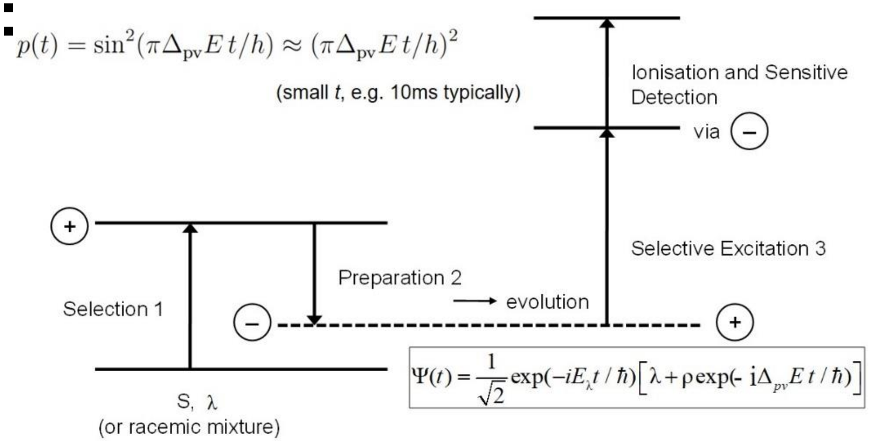
(small t, e.g. 10ms typically)



$$\Psi(t) = \frac{1}{\sqrt{2}} \exp(-iE_\lambda t/\hbar)\left[\lambda + \rho \exp(-\,i\Delta_{pv} E\, t/\hbar)\right]$$

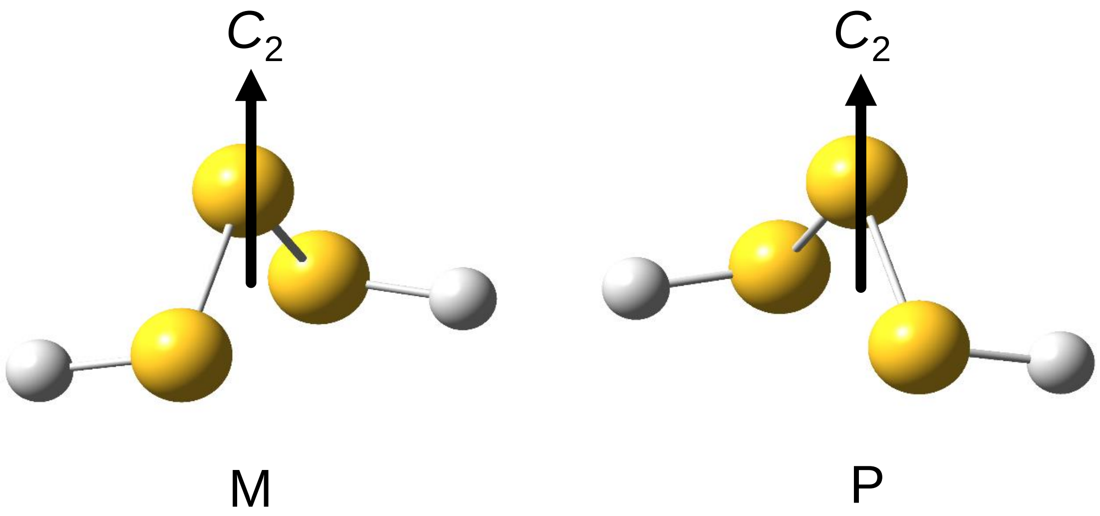
M. Quack, *Chem. Phys. Lett*. **132**, 147 (1986)
-Basic scheme
P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider and G. Seyfang, *J. Chem. Phys*. **143**, 244305 (2015)
-Recent test experiment on NH_3 (achiral)
R. Prentner, M. Quack, J. Stohner and M. Willeke, *J. Phys. Chem. A* **119**, 12805–12822 (2015)
-Recent prediction and detailed simulation for experiment on Cl-O-O-Cl

Measuring $\Delta_{PV}E$ step by step:



1. **Calculate the molecular properties and parity violation of the chiral molecule. (Theory)**
2. **Synthesize the chiral molecule. (Chemistry)**
3. **Measure the rotational, rovibrational or rovibronic spectrum of the chiral molecule. (Experimental Spectroscopy)**
4. **Analyze the spectrum to identify the parity states. (Theoretical Spectroscopy, tunneling switching see talk FE04)**
5. **Conduct the pump-dump-probe experiment. (Laser Spectroscopy and Kinetics)**

HSSSH: Candidate for detecting parity violation



parity violation >> tunneling

$$\Delta_{pv}E \approx (hc)\ 10^{-12}\ \mathrm{cm}^{-1} \gg \Delta E_{\pm} \approx (hc)\ 10^{-23}\ \mathrm{cm}^{-1}$$

For computational details, see:

C. Fábri, L. Horny and M. Quack, *ChemPhysChem,* **2015,** 16, 3584-3589

L. Horny and M. Quack, *Mol. Phys*. **2015** 113, 1768-1779 (Parity violation theory).

B. Fehrensen and D. Luckhaus, M. Quack, *Chem. Phys.* **2007**, *338*, 90-105 (tunneling theory).

HSSSH: Previous spectroscopic work

MW:

D. Mauer, G. Winnewisser, K. M. T. Yamada, *J. Mol. Spectrosc.,* 1989, **136**, 380–386.
M. Liedtke*,* A. H. Saleck*,* J. Behrend*,* G. Winnewisser*,* R. Künsch *and* J. Hahn*, Z. Naturforsch.,*1992, **A47***,* 1091–1093*.*
M. Liedtke, A. H. Saleck, K. M. T. Yamada, G. Winnewisser, D. Cremer, E. Kraka, A. Dolgner, J. Hahn, S. Dobos, *J. Phys. Chem.*,1993, **97**, 11204–11210.
M. Liedtke, K. M. T. Yamada, G. Winnewisser, J. Hahn, *J. Mol. Struct.*,1997, **413**, 265–270.

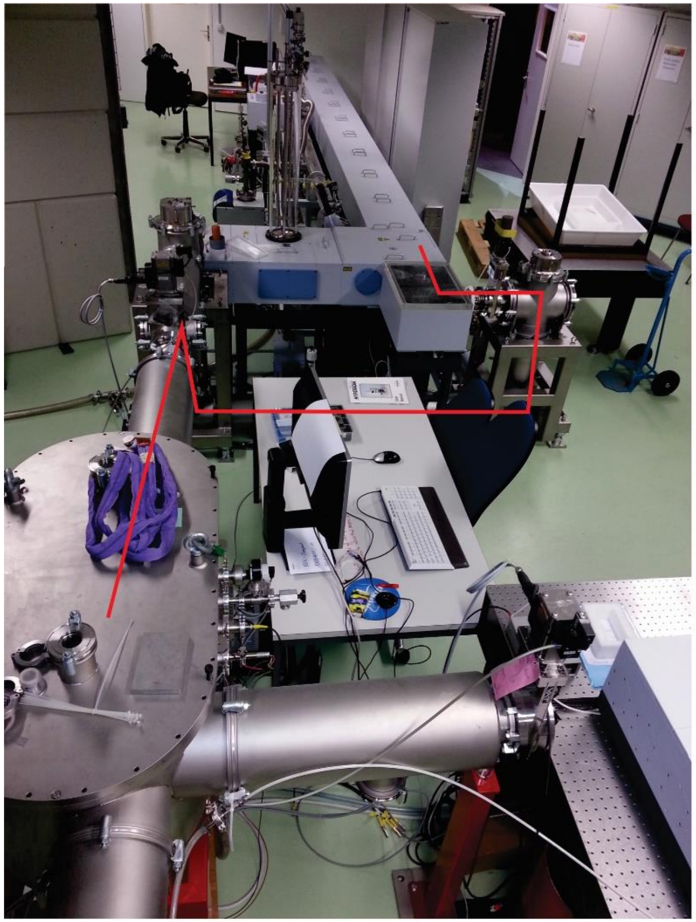
IR (low-resolution)

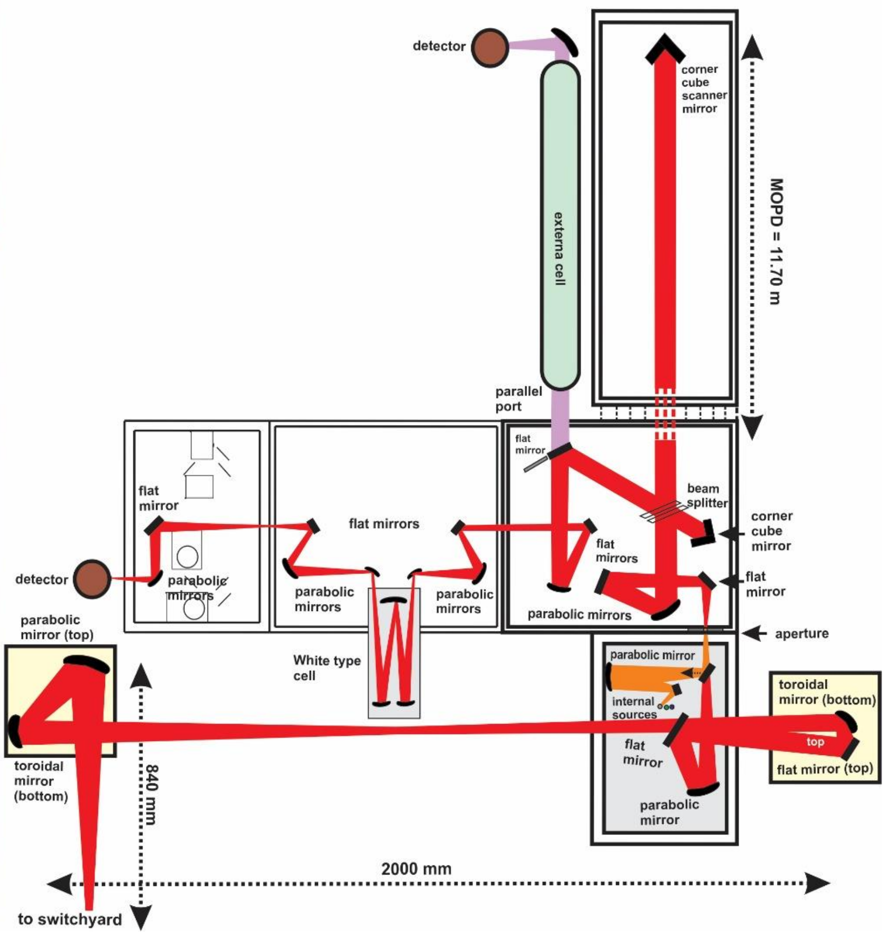
F. Fehér, W. Laue and G. Winkhaus, *Z. Anorg. Allgem. Chem*., 1956, **228**, 113-122.
H. Wieser, P. J. Krueger, E. Muller, J. B. Hyne, *Can. J. Chem.*1969, **47**, 1633–1637.
D. Mauer, G. Winnewisser, K. M. T. Yamada, J. Hahn, K. Reinartz, *Z. Naturforsch. A,* 1988, **43**, 617–620.
D. Mauer, G. Winnewisser, K. M. T. Yamada, *J. Mol. Struct.,* 1988*,* **190**, 457–464.

No high-resolution infrared work available!

High resolution FTIR spectroscopy

unapodized instrument resolution
of 0.00053 cm^{-1} (16 MHz)





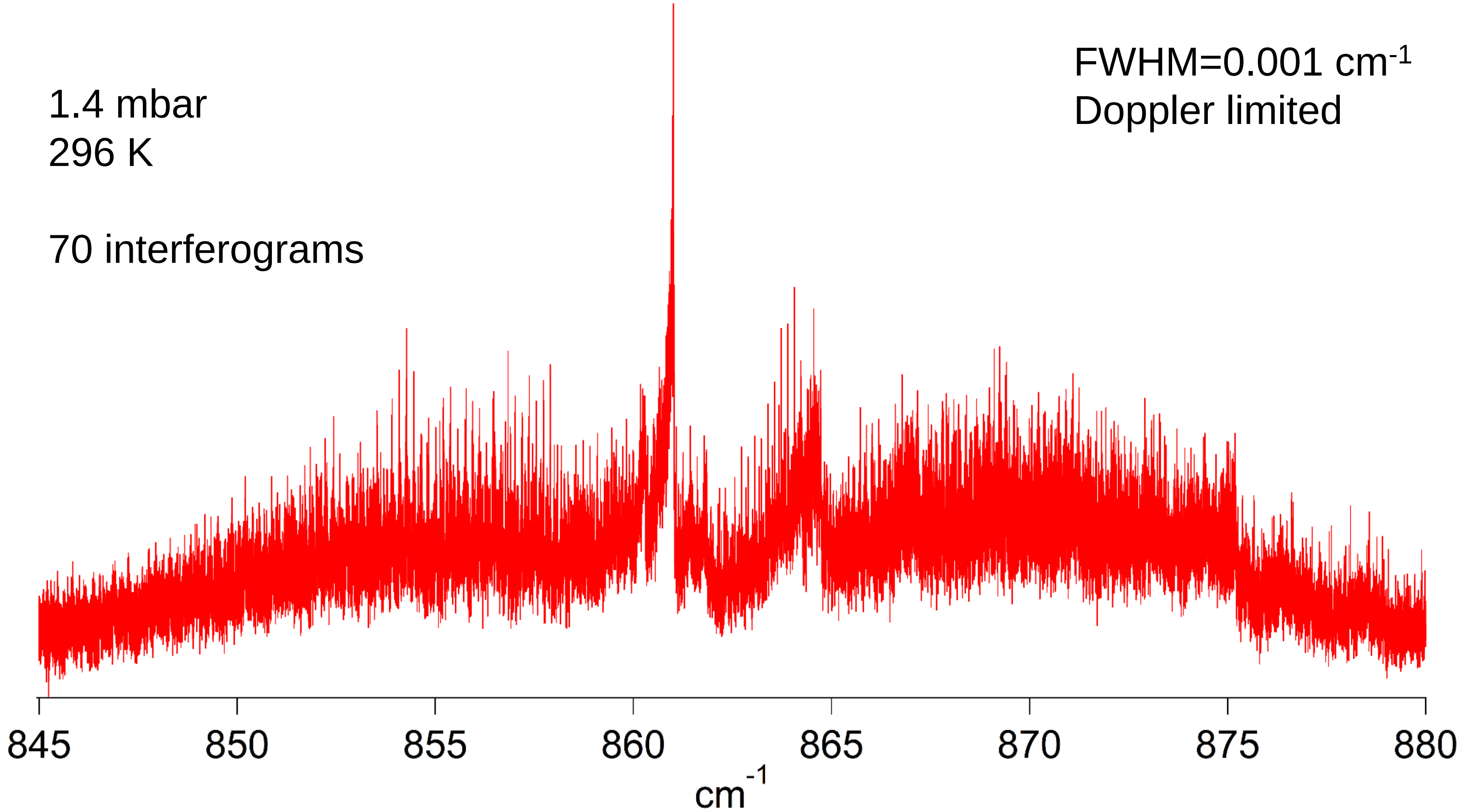
S. Albert, K.K. Albert, Ph. Lerch, M. Quack, *Faraday Discussions*, **150**, 71-99 (2011)
S. Albert, K. K. Albert and M. Quack, *High Resolution Fourier Transform Infrared Spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 2 (Eds. M. Quack and F. Merkt), John Wiley & Sons, Ltd, Chichester, pp. 965-1019 (2011)
S. Albert, Ph. Lerch and M. Quack, *Chem. Phys. Chem. 14,* 3204-3208 (2013)

Bands between 845 and 880 cm^{-1}

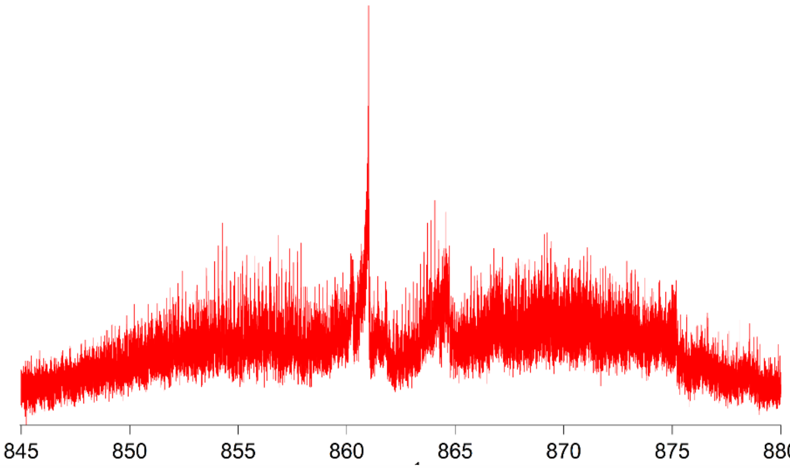
1.4 mbar
296 K

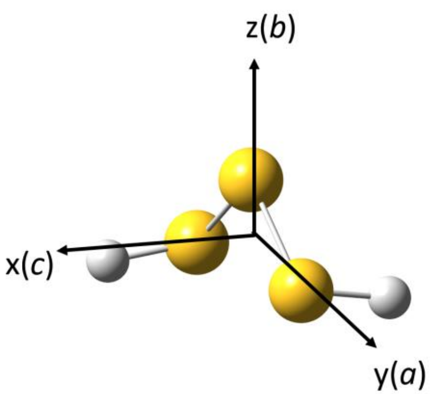
70 interferograms

FWHM=0.001 cm^{-1}
Doppler limited



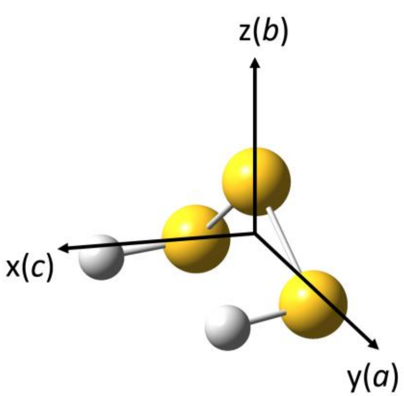
Bands between 845 and 880 cm^{-1}





trans (P)

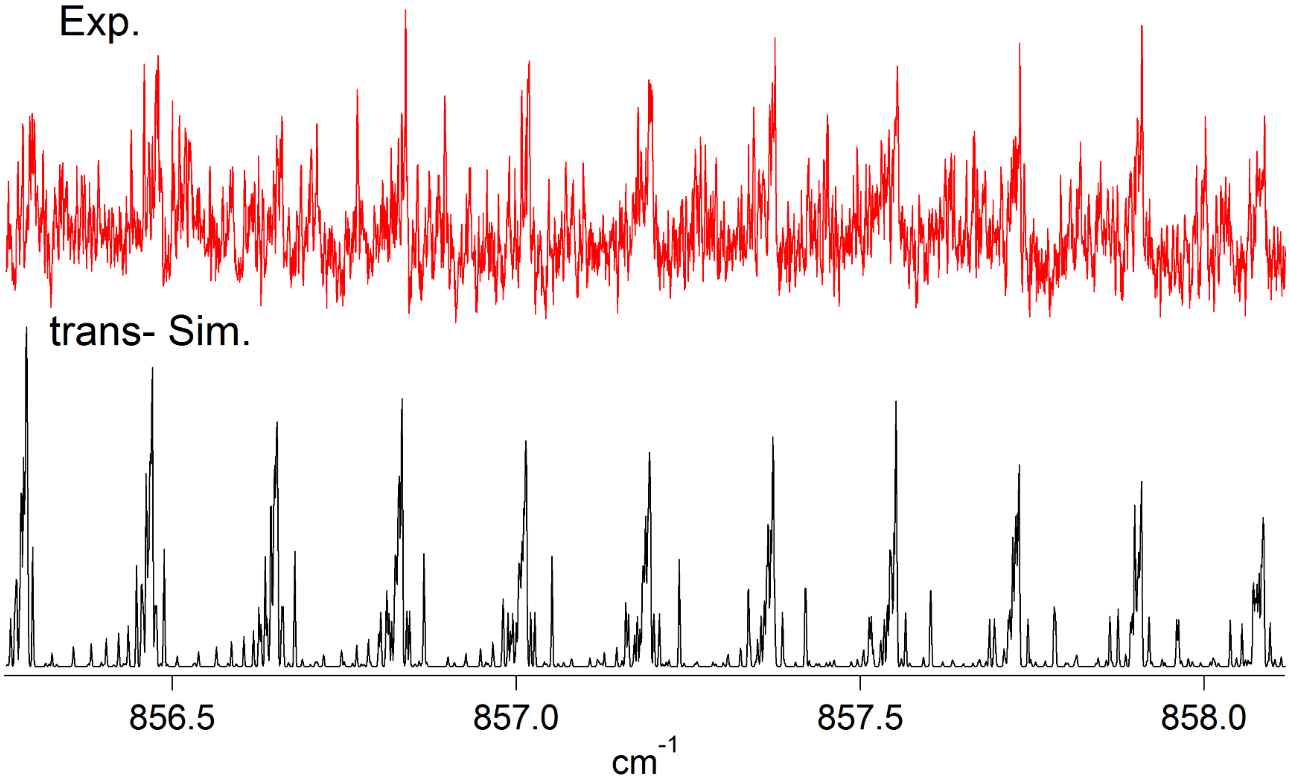
	fundamental	Γ	$\tilde{\nu}$ / cm-1	μ /Debye	Type
1	s SH stretch	A	2622.498	-0.004	*b*
2	s SSH bend	A	871.64	-0.004	*b*
3	s SS stretch	A	501.975	-0.017	*b*
4	s torsion	A	300.338	0.162	*b*
5	SSS bend	A	206.009	-0.003	*b*
6	as SH stretch	B	2621.73	0.002/-0.001	*a/c*
7	as SSH bend	B	860.564	-0.054/-0.032	*a/c*
8	as SS stretch	B	496.743	0.130/-0.011	*a/c*
9	as torsion	B	324.669	-0.132/0.033	*a/c*



cis

	fundamental	Γ	$\tilde{\nu}$ / cm-1	μ /Debye	Type
1	s SH stretch	A\`	2616.057	0.007/0.009	*b/c*
2	s SSH bend	A\`	874.056	-0.002/-0.039	*b/c*
3	s SS stretch	A\`	502.778	0.018/0.002	*b/c*
4	s torsion	A\`	325.212	0.131/-0.035	*b/c*
5	SSS bend	A\`	206.899	-0.004/-0.009	*b/c*
6	as SH stretch	A\`\`	2619.507	-0.003	*a*
7	as SSH bend	A\`\`	864.807	-0.052	*a*
8	as SS stretch	A\`\`	497.561	-0.135	*a*
9	as torsion	A\`\`	309.145	0.107	*a*

The ν_7 fundamental of HSSSH



a-type transitions

	This study (GSCD)	*trans* MW[a]	*trans*[b]	*cis* MW[a]	*cis*[b]
A/MHz	14 120 (25)	14098.89950 (30)	13 802	14103.20771 (17)	13 796
B/MHz	2750.15 (22)	2750.15267 (16)	2734	2752.759027 (81)	2737
C/MHz	2371.57 (20)	2371.69686 (86)	2347	2373.869384 (86)	2350

[a] M. Liedtke, K. M. T. Yamada, G. Winnewisser, J. Hahn, *J. Mol. Struct.*,1997, **413**, 265–270.
[b] C. Fábri, L. Horny and M. Quack, *ChemPhysChem,* **2015,** 16, 3584-3589

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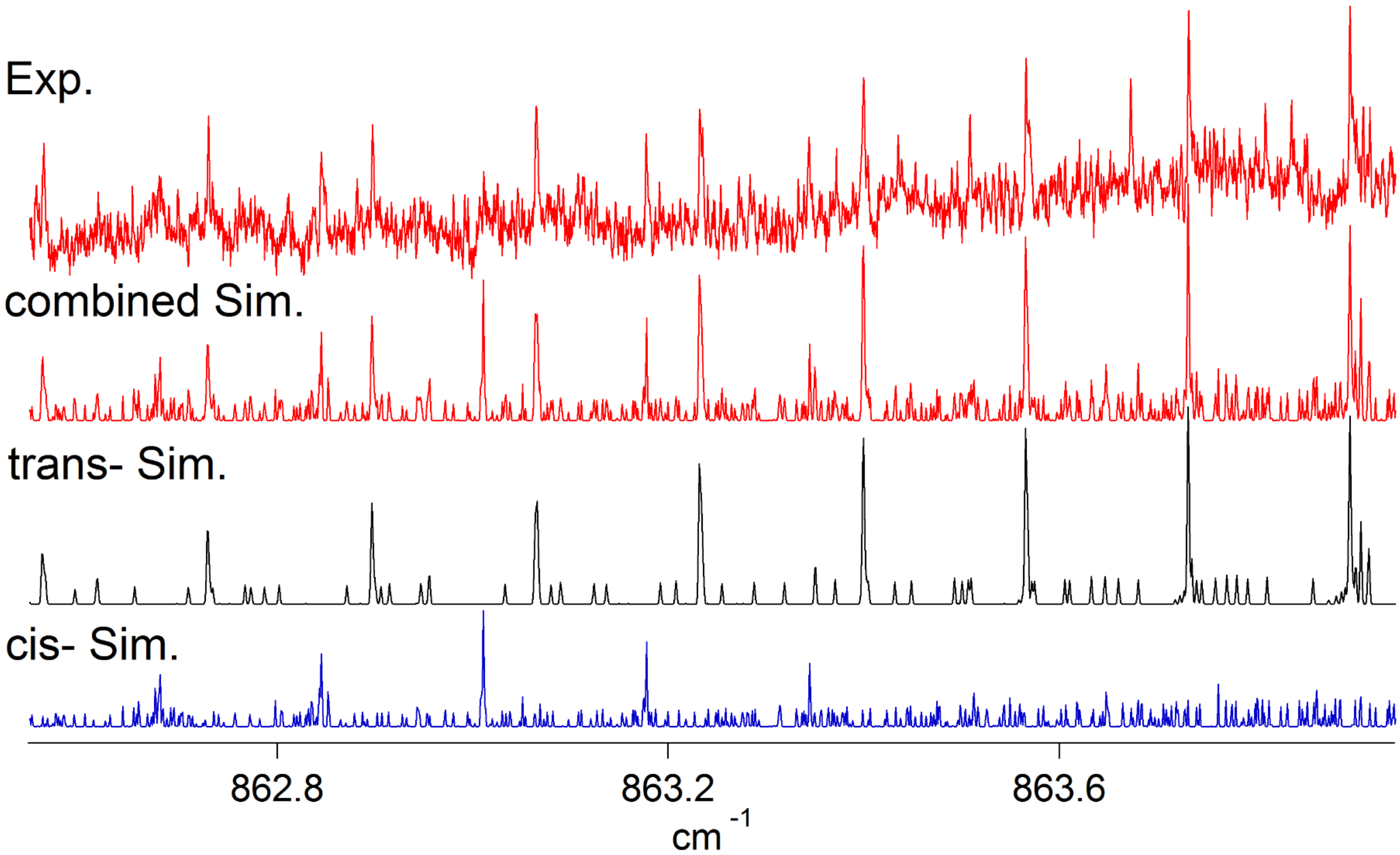

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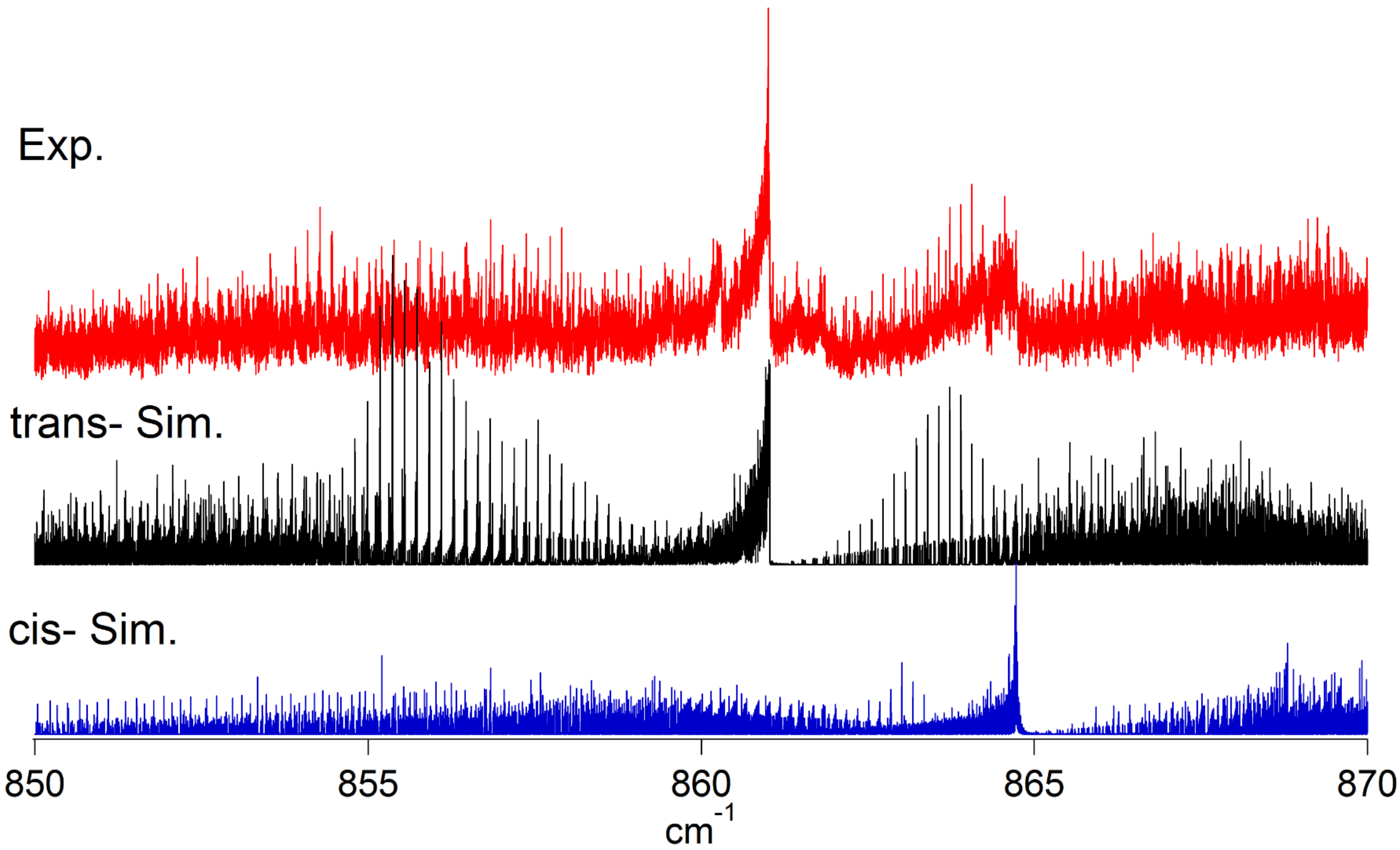
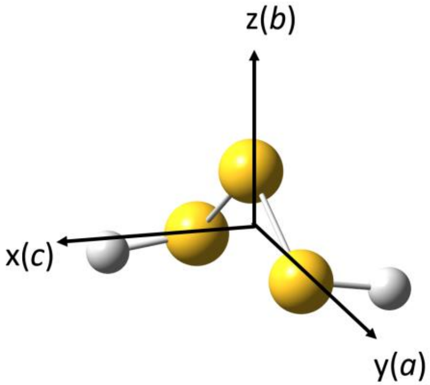
The ν_7 fundamental of HSSSH

assymetric -SSH bending



What’s next?

Synchrotron-based FTIR in the far-IR region already underway



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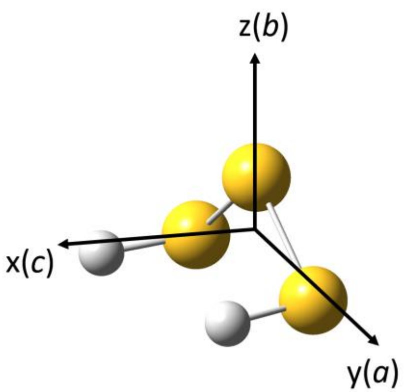

cis

	fundamental	Γ	$\tilde{\nu}$ / cm-1	μ /Debye	Type
1	s SH stretch	A`	2616.057	0.007/0.009	*b/c*
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8	as SS stretch	A``	497.561	-0.135	*a*
9	as torsion	A``	309.145	0.107	*a*

Conclusion

HSSSH is a chiral molecule which may be a good candidate to measure the parity violating energy difference $\Delta_{pv}E$ between the enantiomers

We measured the first high resolution FTIR spectrum and the initial analyses were successful

Acknowledgement

- The group of Martin Quack at ETH Zürich: www.ir.ETHz.ch

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SWISS NATIONAL SCIENCE FOUNDATION

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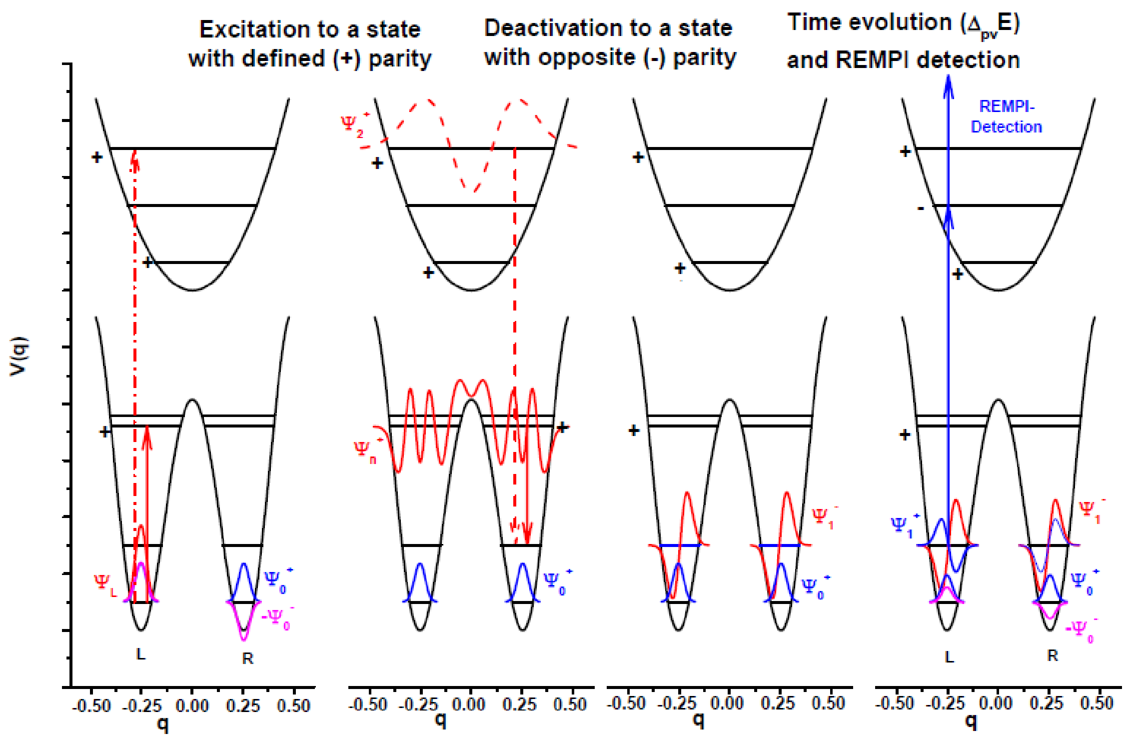
European Research Council

Four steps to detect parity violation (experimental test on NH_3)

P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider and G. Seyfang, *J. Chem. Phys*., 143, 244305 (2015)



- **Search for levels showing tunneling switching at 2400 cm^{-1} where parity (+, –) is defined.**
- **Carry out the Selection-Preparation-Evolution-Detection scheme.**
- **Test experiments on NH_3 show sensitivity to be sufficient to measure $\Delta_{PV}E \geq 100$ aeV.**

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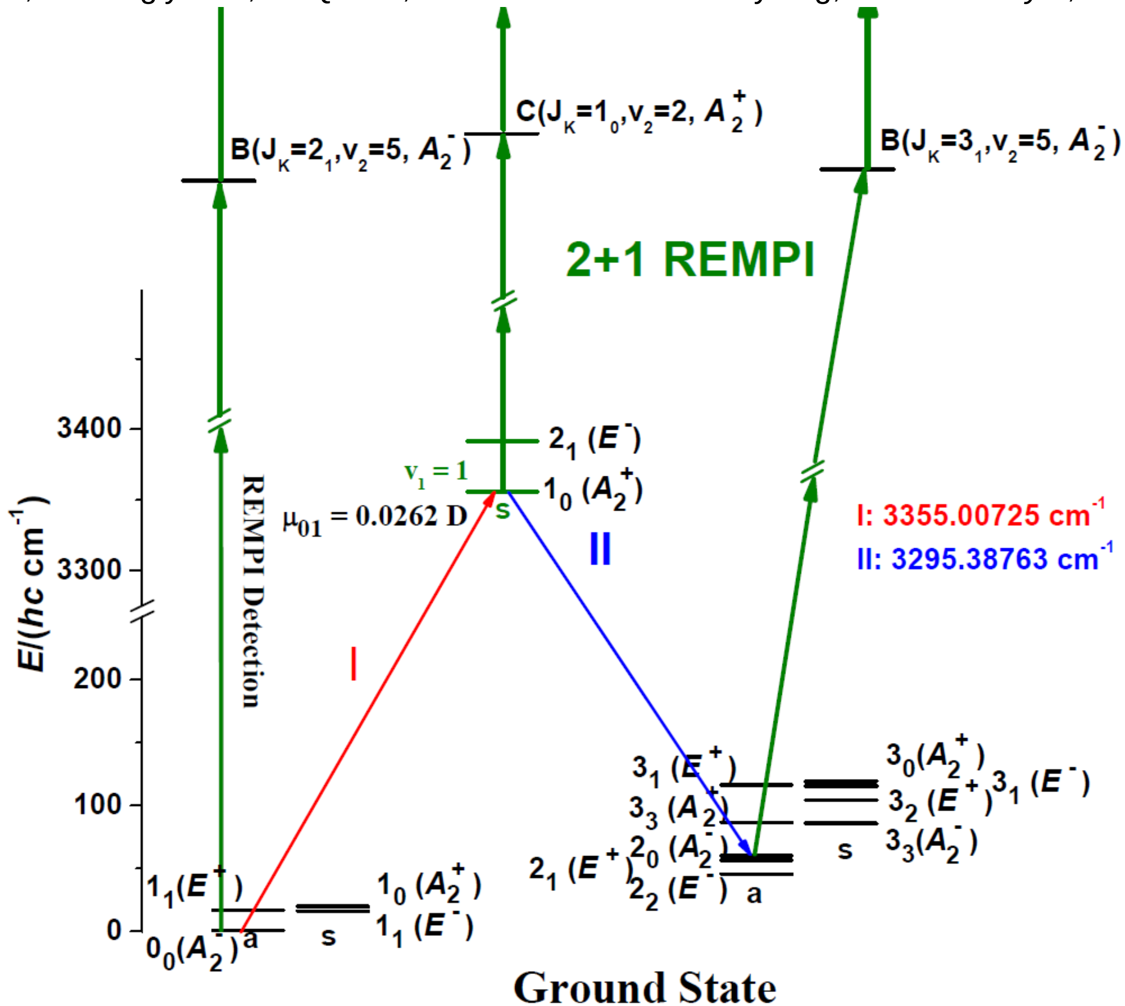
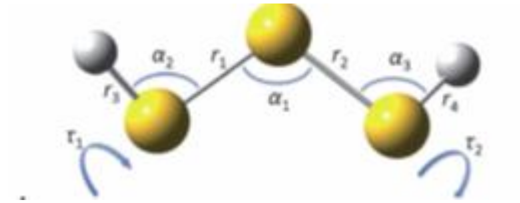
Selection-Preparation-Evolution-Detection experiment: NH_3 (achiral)

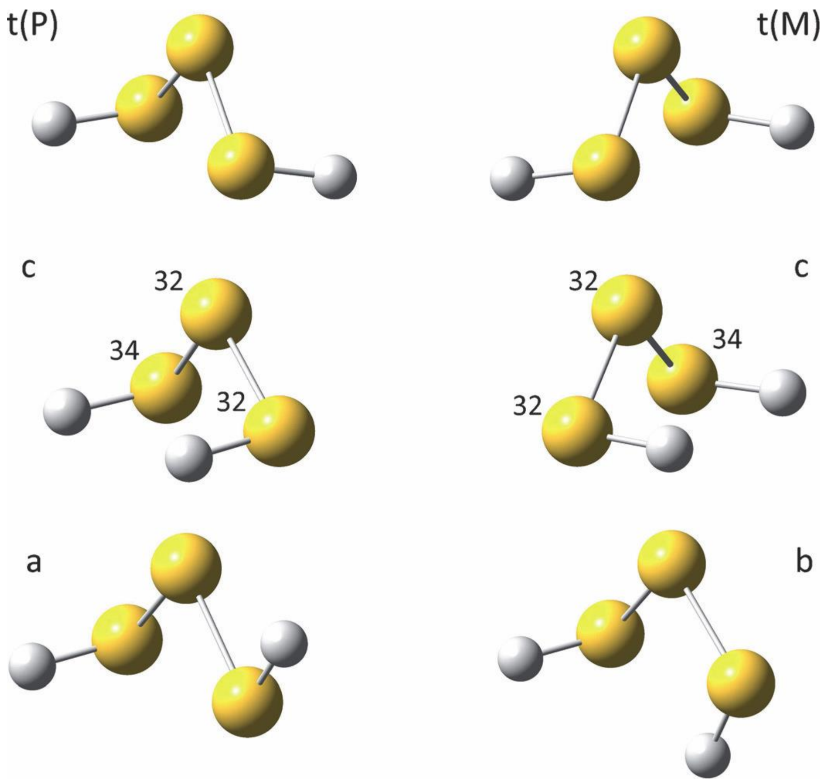
P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider and G. Seyfang, *J. Chem. Phys.*, 143, 244305 (2015)

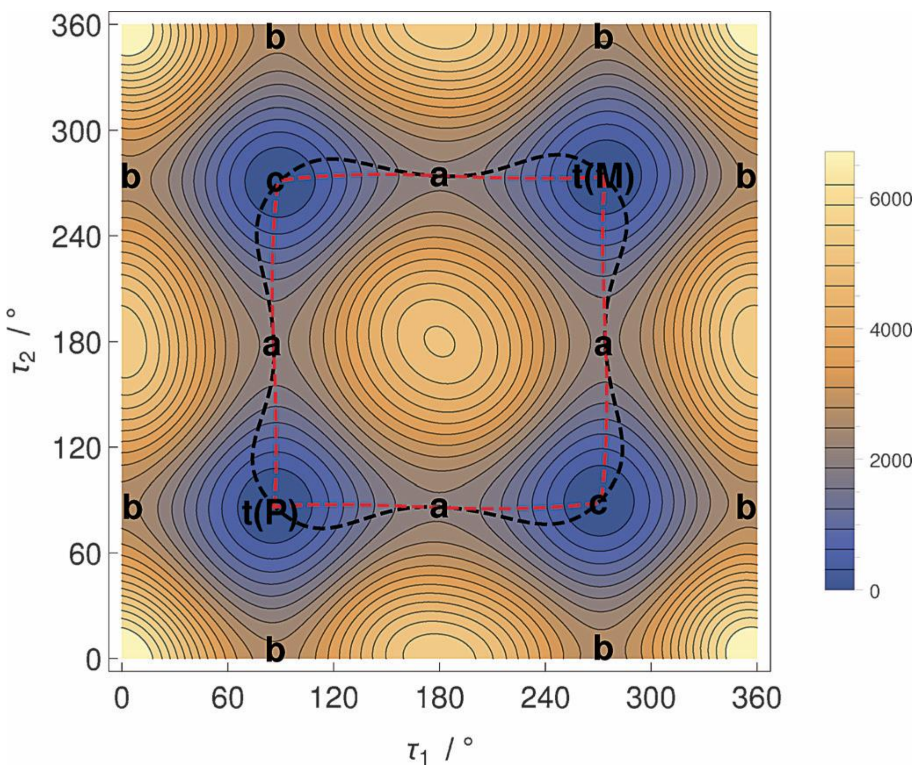


Proven sensitivity in principle sufficient to detect evolution in about 10 ms time (1m time of flight) with $\Delta_{PV}E$ > 100 aeV

HSSSH: Theoretical work







C. Fábri, L. Horny and M. Quack, *ChemPhysChem,* **2015,** 16, 3584-3589