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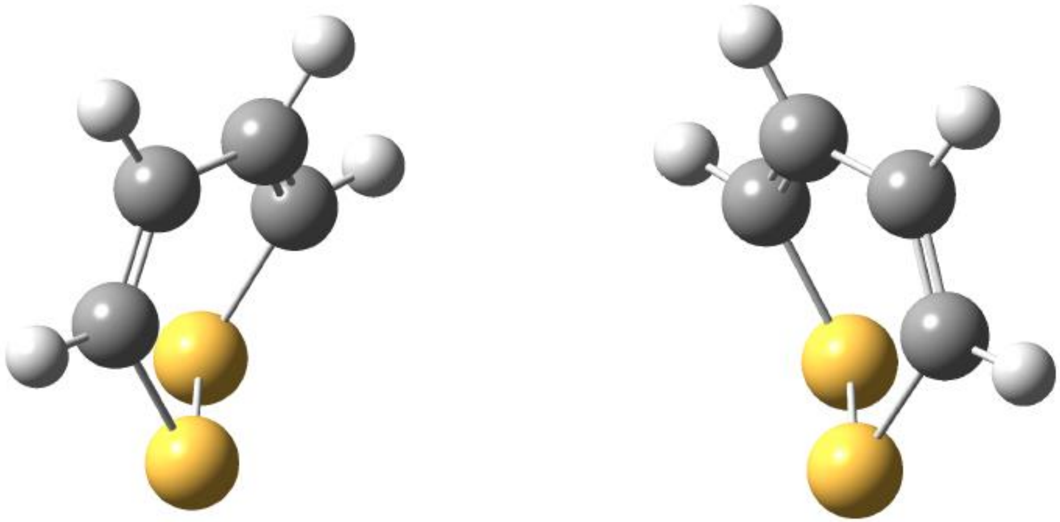

HIGH RESOLUTION GIGAHERTZ AND TERAHERTZ (FTIR) SPECTROSCOPY AND THEORY OF PARITY VIOLATION AND TUNNELING FOR 1,2-DITHIINE ($C_4H_4S_2$) AS A CANDIDATE FOR MEASURING THE PARITY VIOLATING ENERGY DIFFERENCE BETWEEN ENANTIOMERS OF CHIRAL MOLECULES

S. Albert,[1, 2] I. Bolotova,[1] Z. Chen,[1] C. Fábri,[1] L. Horny,[1] M. Quack,[1] G. Seyfang[1] and D. Zindel[1] (*Phys. Chem. Chem. Phys.,* (2016) *in press,* DOI:10.1039/c6cp01493c)

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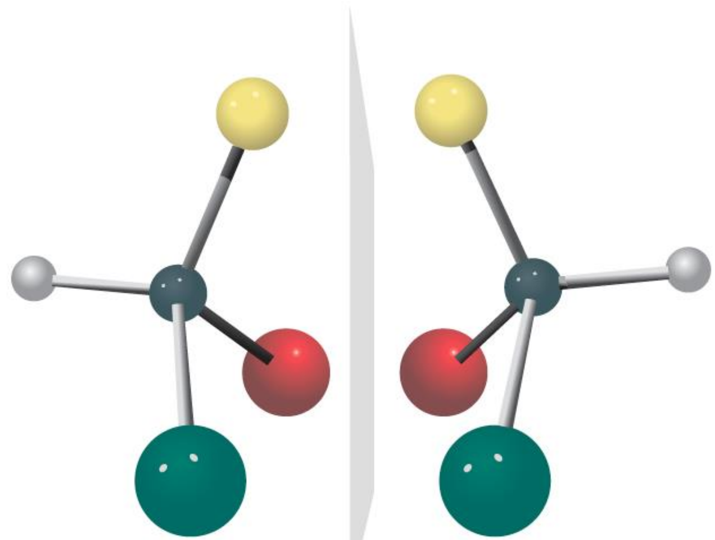
Energy difference in enantiomers of a chiral molecule

Traditional theory:

van‘t Hoff 1887

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

exactly by symmetry



R S

Today:

electroweak parity violation

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

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

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

Example : CHBrClF

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

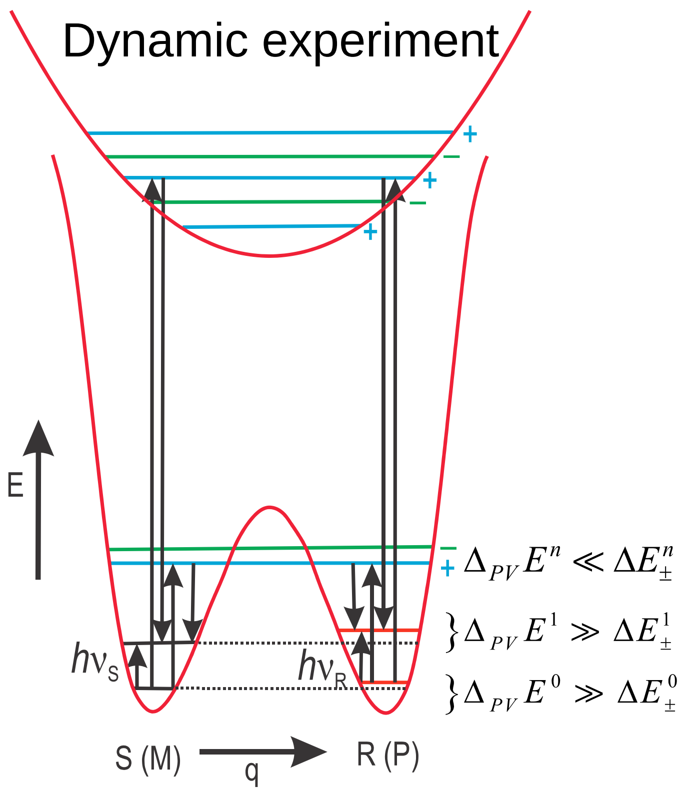
Schemes to measure molecular parity violation

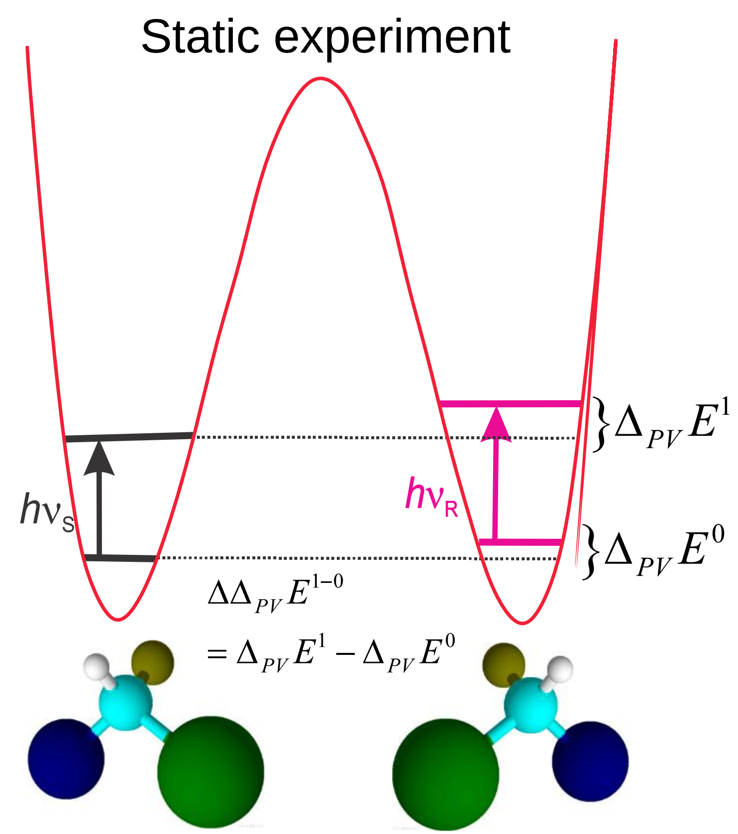
M. Quack, *Chem. Phys. Lett*. 132, 147 (1986);
M. Quack, *Angew.Chem.Int.Ed.* 28,571 (1989)

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)



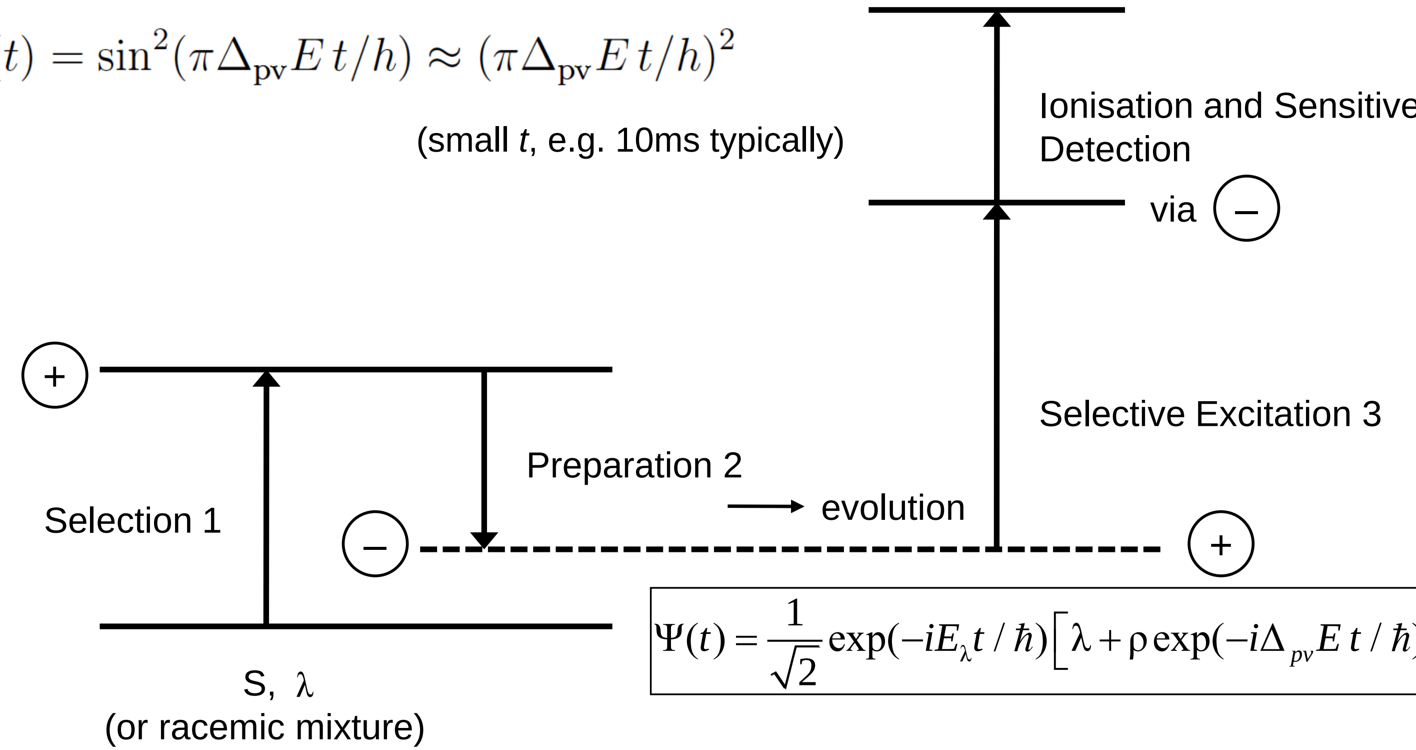


Review: M. Quack, in “Handbook of High-Resolution Spectroscopy”, Vol.1, Chapter 18, 659–722, M. Quack and F. Merkt, Eds., Wiley, Chichester,2011.

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

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

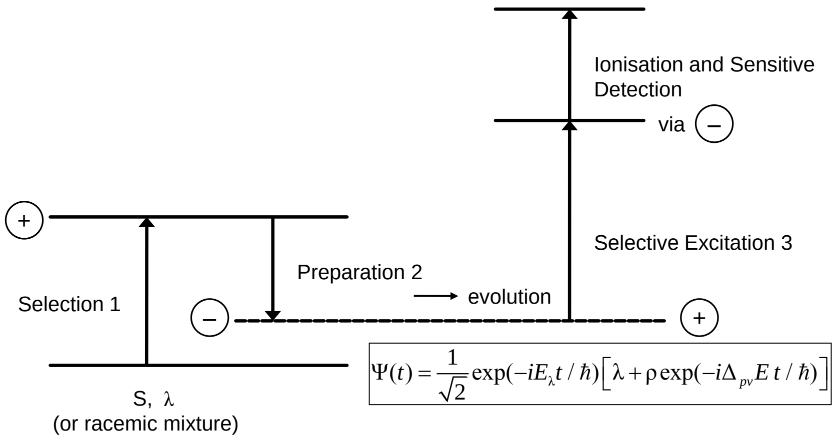
(small *t*, e.g. 10ms typically)



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

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 detaiend 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)**

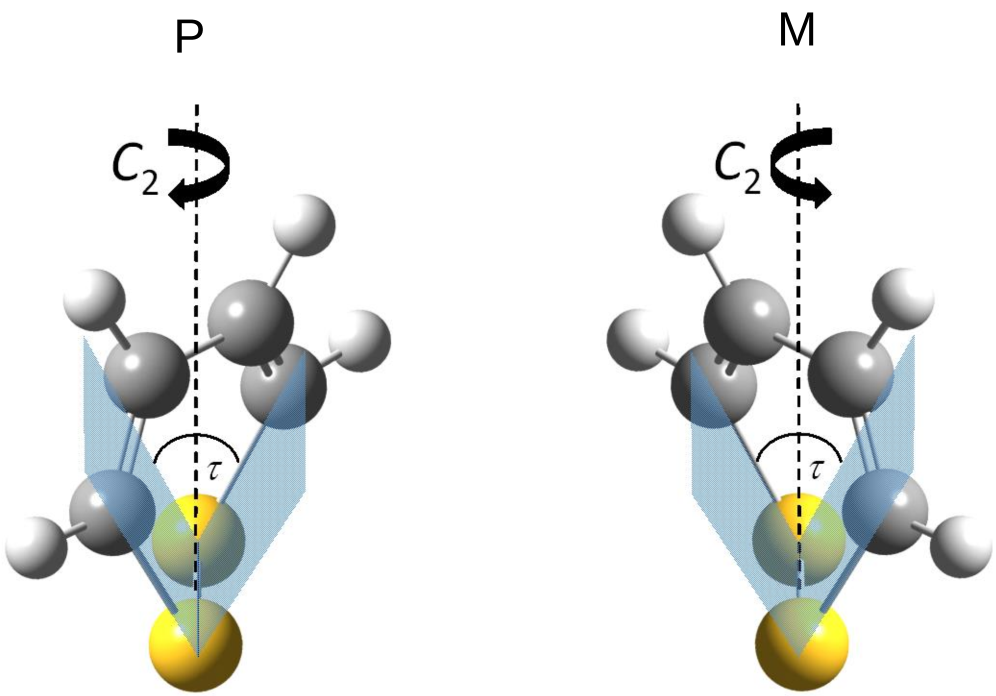
2. **Synthesize the chiral molecule. (Chemistry)**

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)**

1, 2-dithiine: Candidate for detecting parity violation

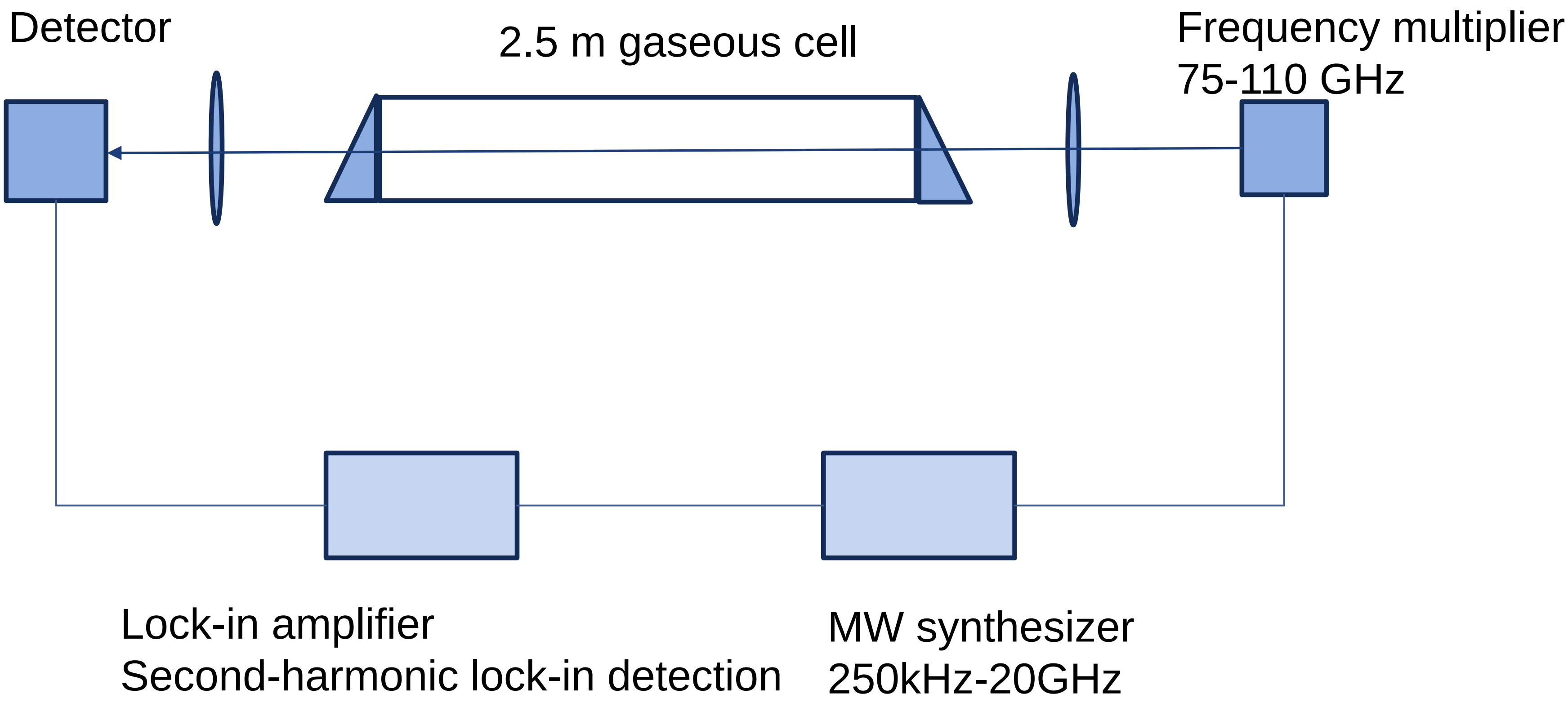


parity violation >> tunneling

$$\Delta_{pv}E \approx (hc)\ 10^{-11}\ \text{cm}^{-1} \gg \Delta E_{\pm} \approx (hc)\ 10^{-25}\ \text{cm}^{-1}$$

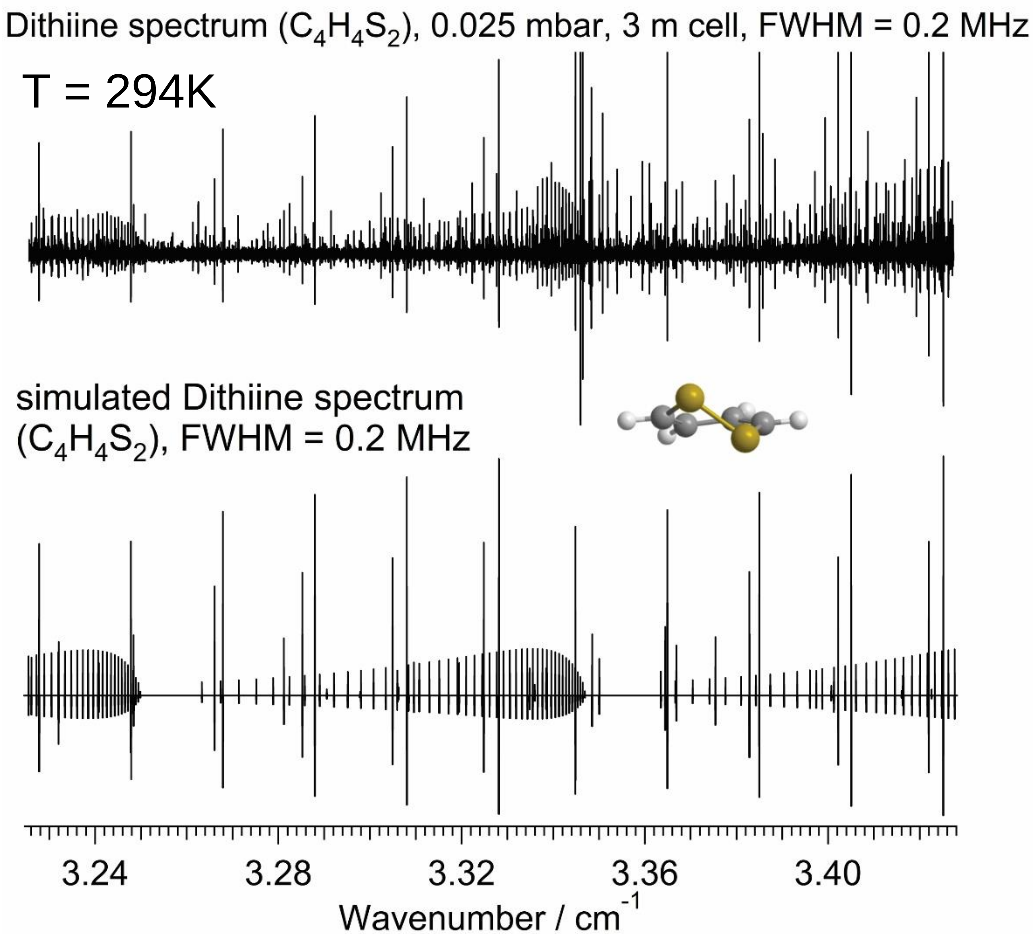
S. Albert, I. Bolotova, Z. Chen, C. Fábri, L. Horny, M. Quack, G. Seyfang and D. Zindel, *Phys. Chem. Chem. Phys.,* **2016** *in press,* DOI:10.1039/c6cp01493c
L. Horny and M. Quack, *Mol. Phys*. **2015** 113, 1768-1779 (Parity violation theory).
B. Fehrensen and D. Luckhaus, M. Quack, *Chem. Phys.* **2007**, *338*, 90-105 (tunneling theory).

GHz spectroscopy



M. Suter and M. Quack, *Appl. Opt* **54**, 4417-4431 (2015)

GHz spectroscopy: rotational transitions in the ground state

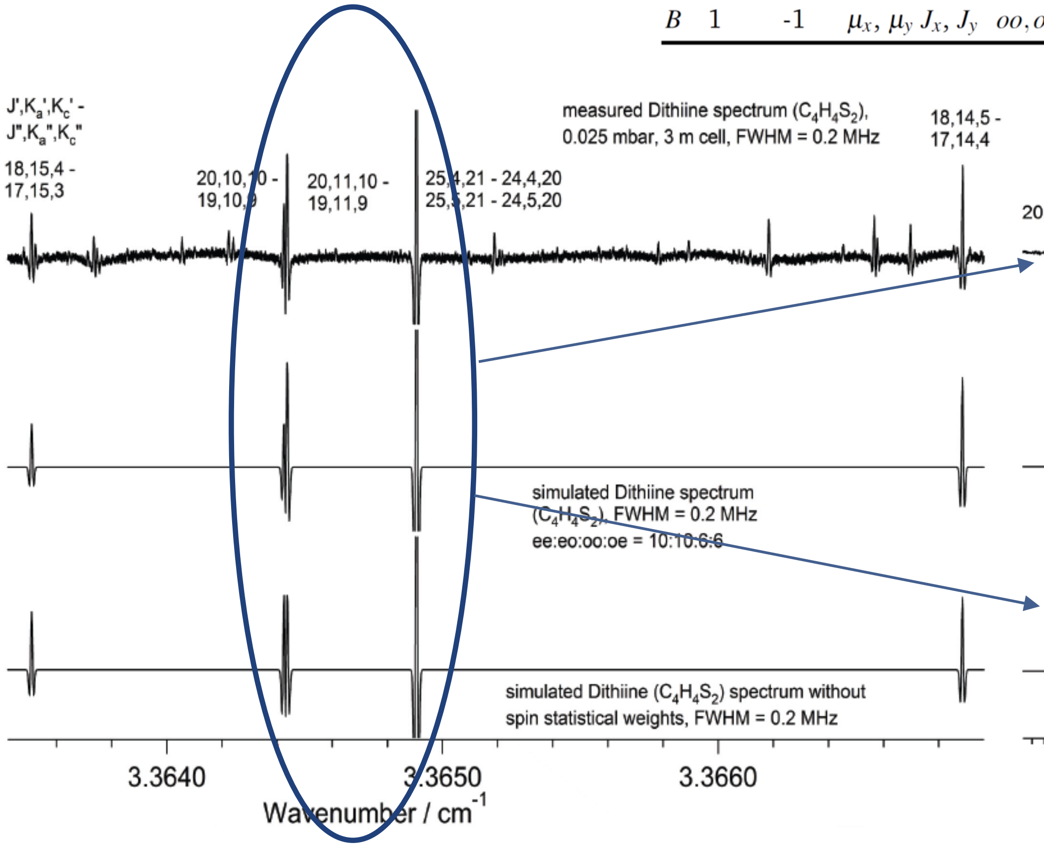


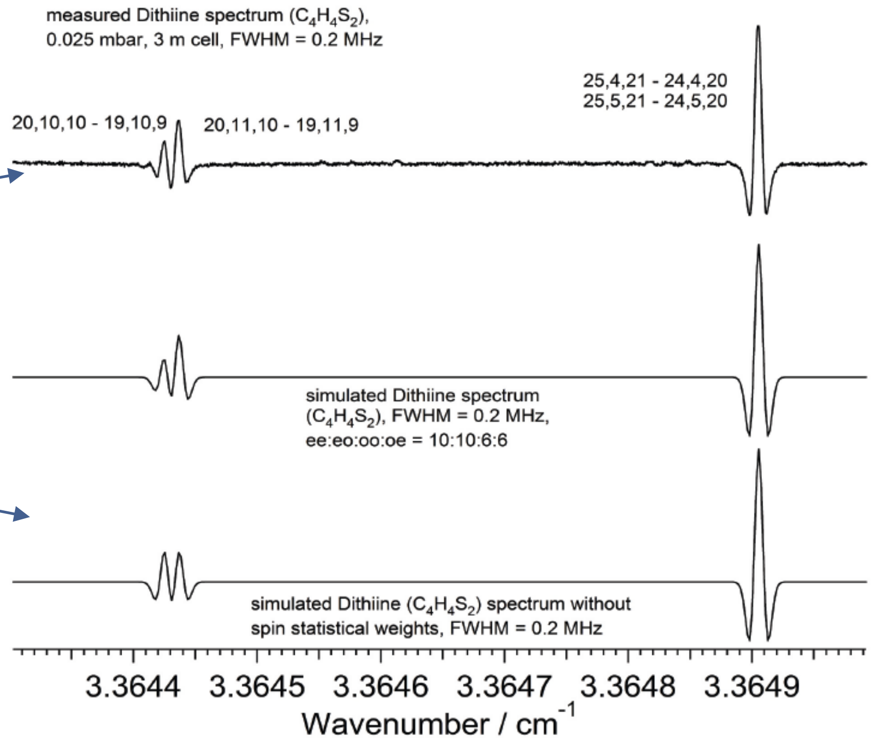
Previous microwave work: 15 lines
(J.Z. Gillies, C.W. Gillies. E. A. Cotter, E. Block and R. DeOrazio, *J. Mol. Spectrosc.*, **180**, 139-144 (1996))

Present work: 560 lines
(S. Albert, I. Bolotova, Z. Chen, C. Fábri, L. Horny, M. Quack, G. Seyfang and D. Zindel, *Phys. Chem. Chem. Phys.*, **2016** *in press*, DOI:10.1039/c6cp01493c)

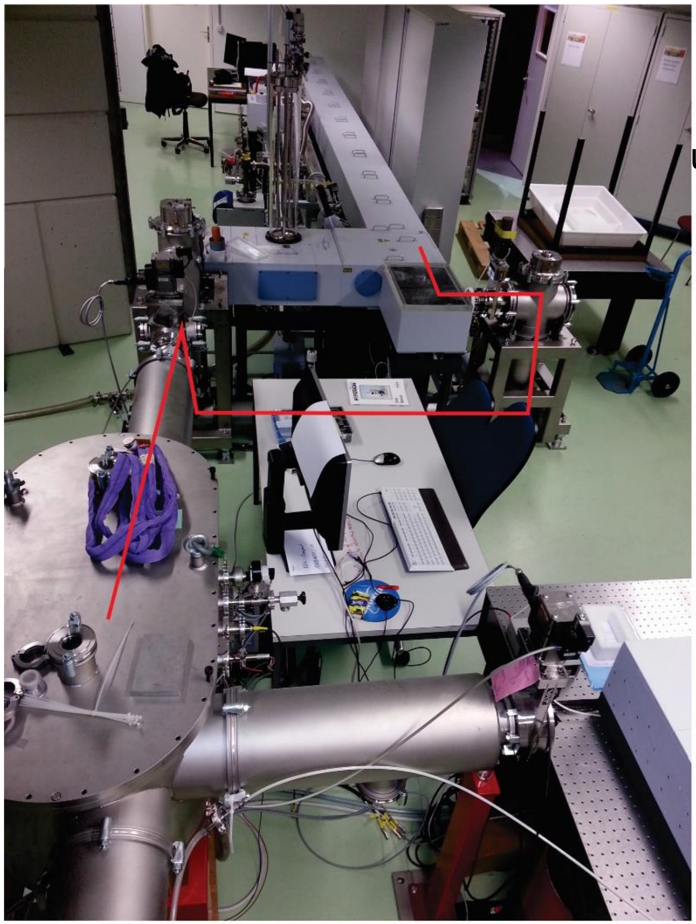
GHz spectroscopy: rotational transitions in the ground state

C_2	E	C_2 $(\alpha\beta)$	μ	J	K_aK_c	n_{Γ_V}	n_{Γ_S}	g
A	1	1	μ_z	J_z	ee, eo	13	10	10
B	1	-1	μ_x, μ_y	J_x, J_y	oo, oe	11	6	6

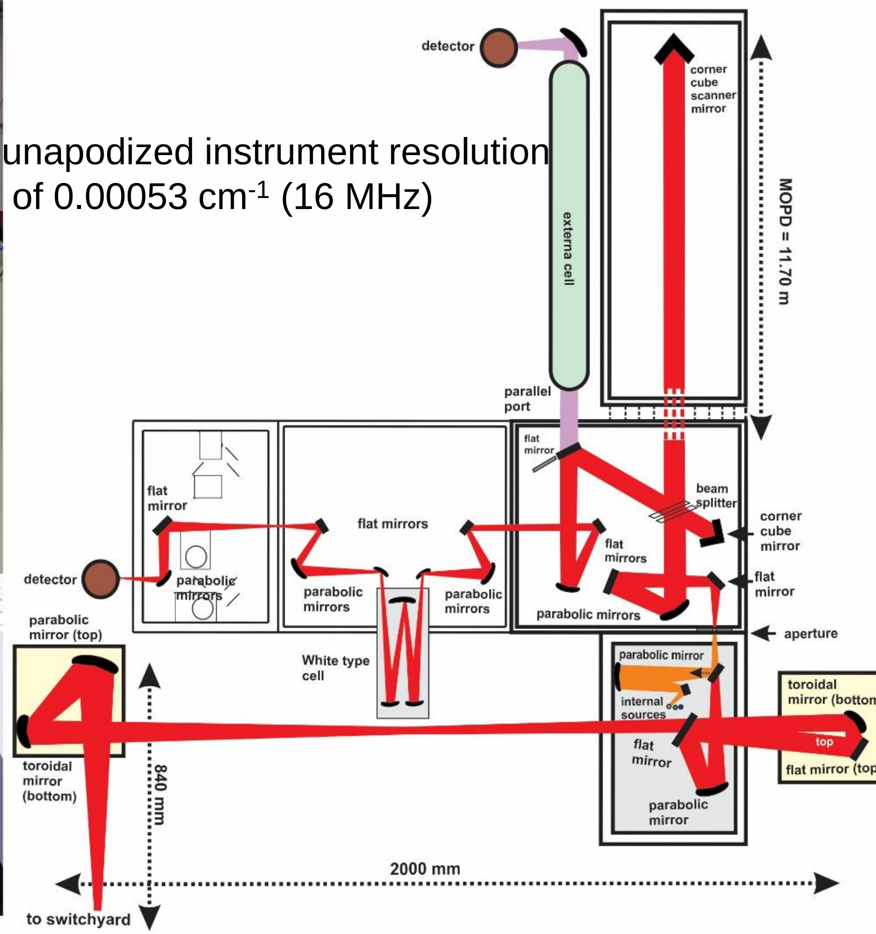




High resolution FTIR spectroscopy

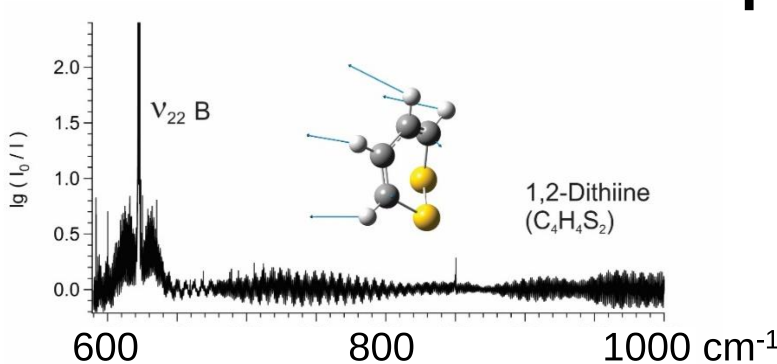


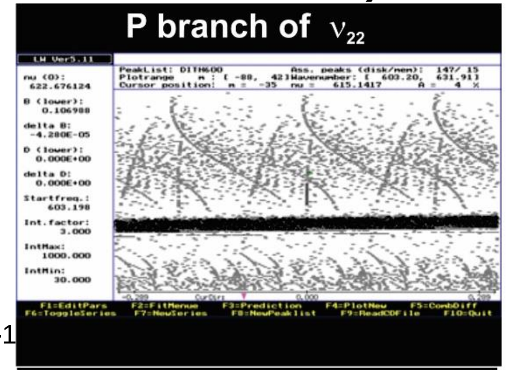
unapodized instrument resolution of 0.00053 cm^{-1} (16 MHz)

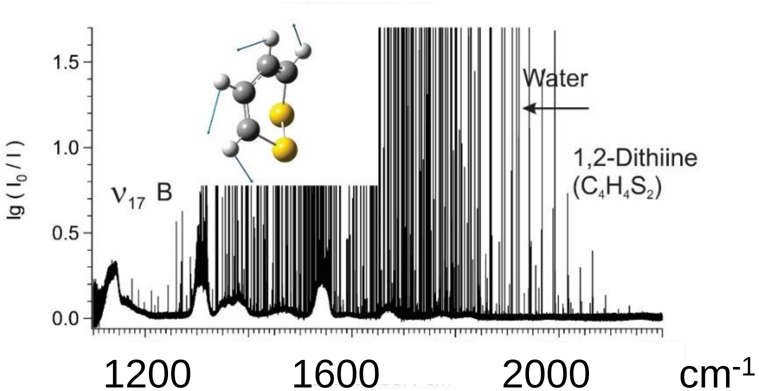


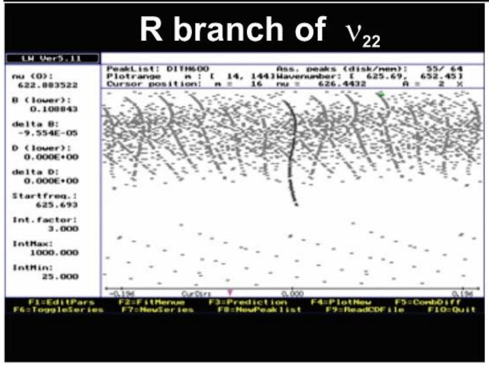
S. Albert, K.K. Albert, Ph. Lerch, M. Quack, *Faraday Discussions*, **150**, 71-99 (2011)
S. Albert, K. K. Albert and M. Quack, *High Resolution Fourier Transform Infrared Spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 2 (Eds. M. Quack and F. Merkt), John Wiley & Sons, Ltd, Chichester,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

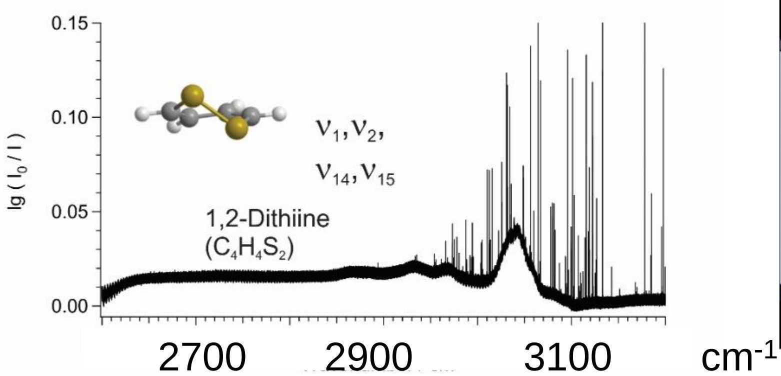
Overview of the FTIR spectrum of 1,2-dithiine

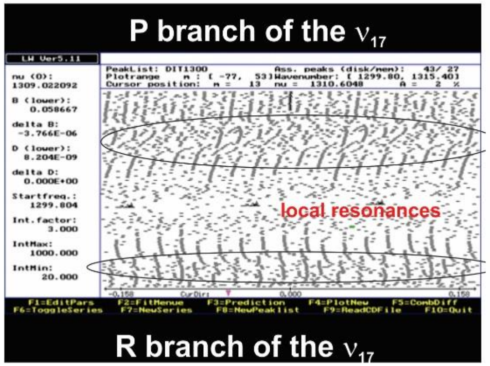




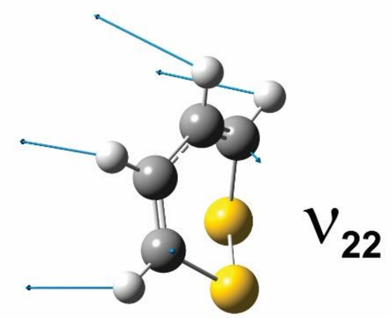




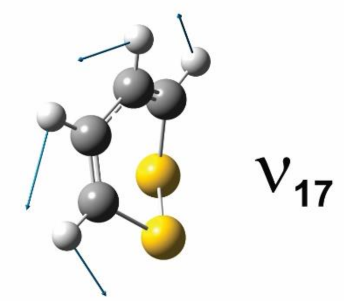




$\tilde{\nu}_{22} = 623.094\ cm^{-1}$



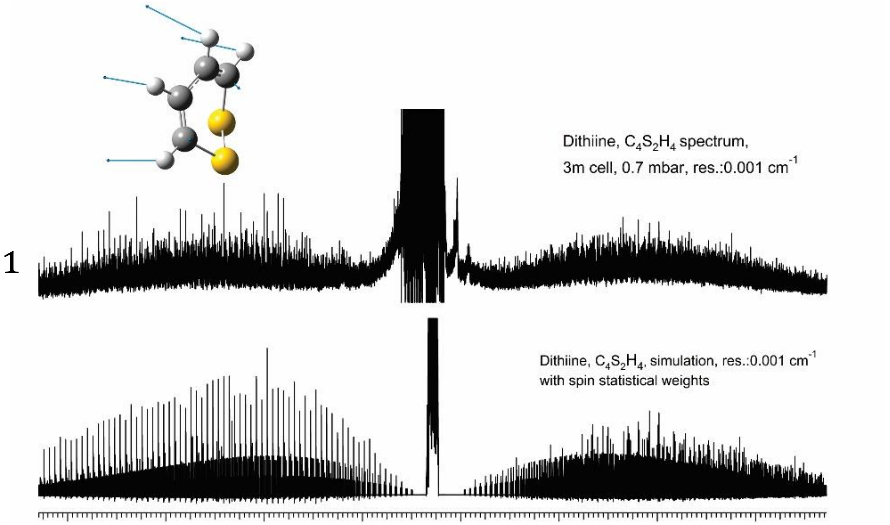
$\tilde{\nu}_{17} = 1308.873\ cm^{-1}$

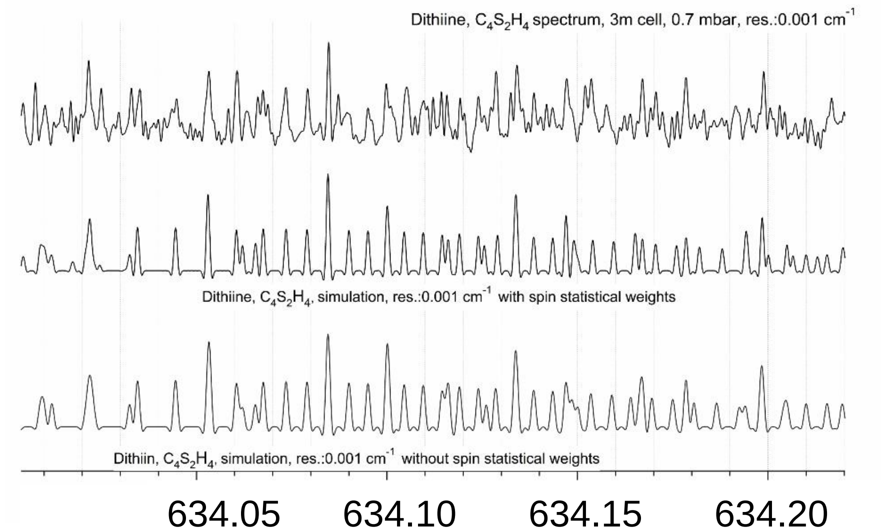


The ν_{22} fundamental of 1,2-dithiine

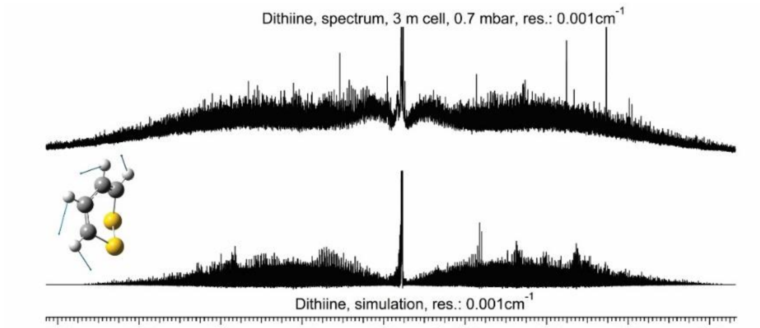
-CH out-of-plane bending

$$\tilde{\nu}_{22} = 623.094\ cm^{-1}$$

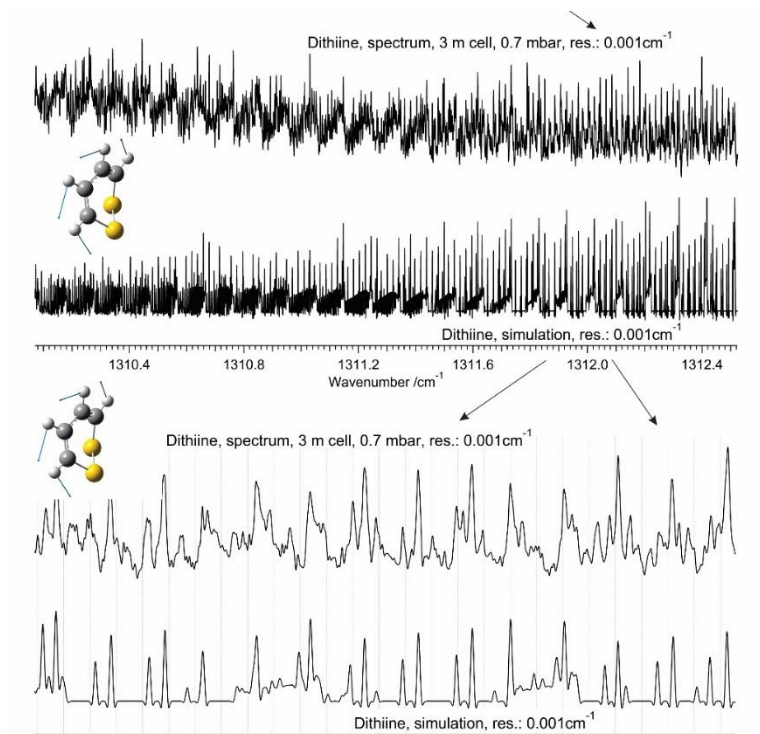




The ν_{17} fundamental of 1,2-dithiine



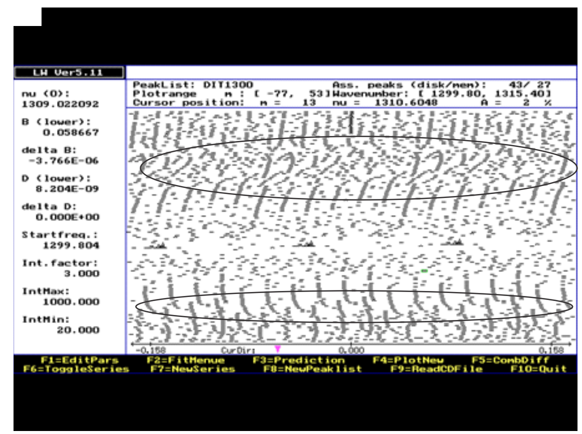
1292 1308 1324 cm^{-1}

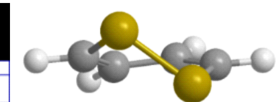


1311.95 1312.05 1312.15 cm^{-1}

-CH in-plane bending

$$\tilde{\nu}_{17} = 1308.873\ cm^{-1}$$



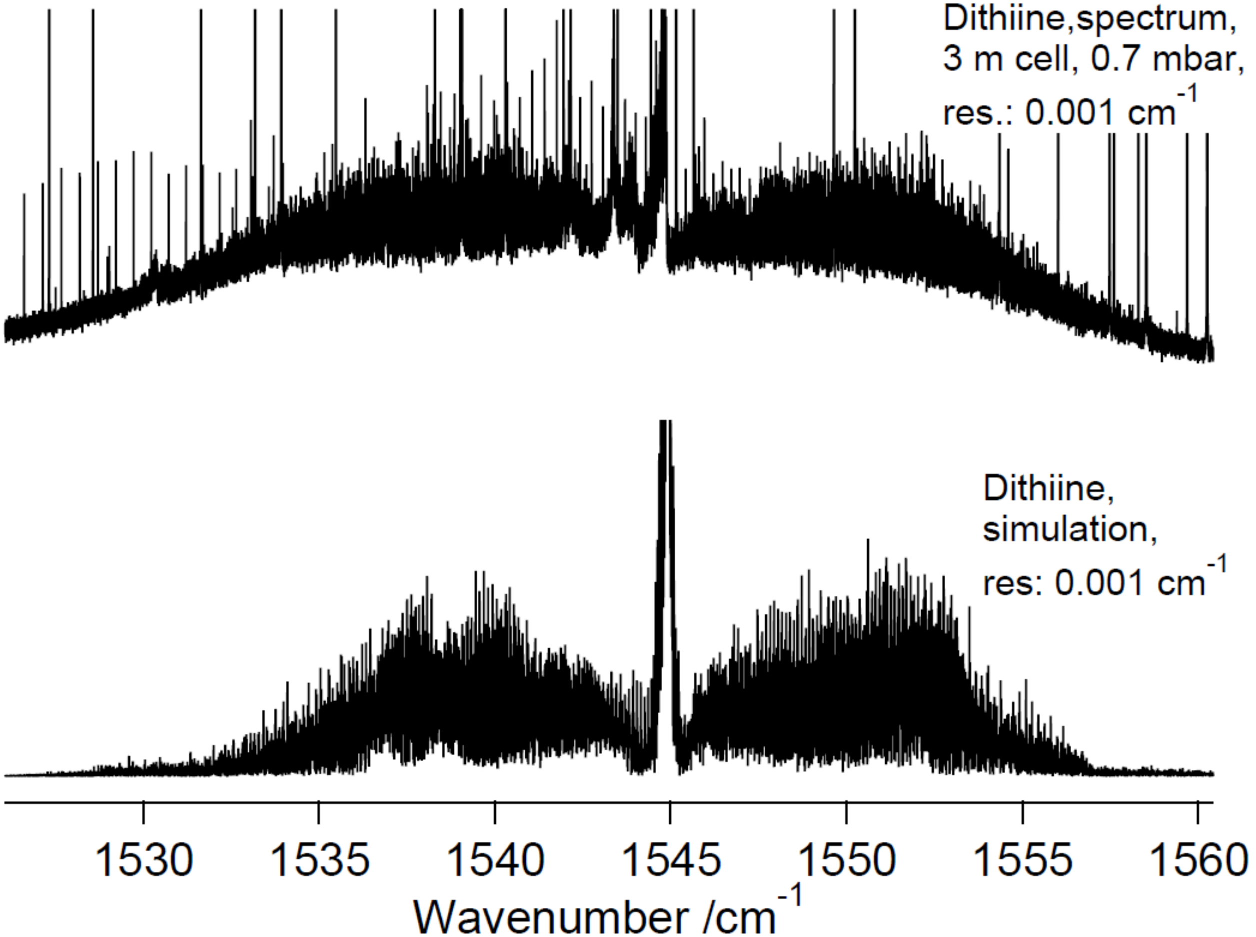


P branch of the ν_{17} fundamental

local resonances

R branch of the ν_{17} fundamental

The ν_3 fundamental of 1,2-dithiine

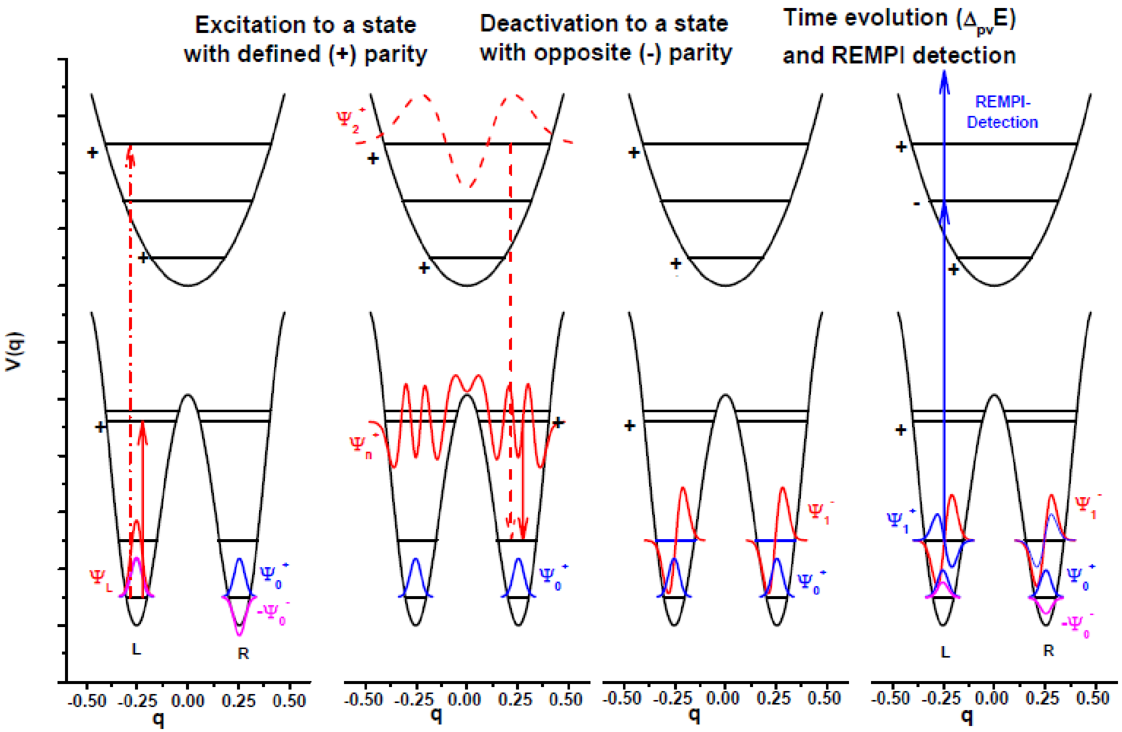


-CC stretching

$$\tilde{\nu}_3 = 1544.900\ cm^{-1}$$

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

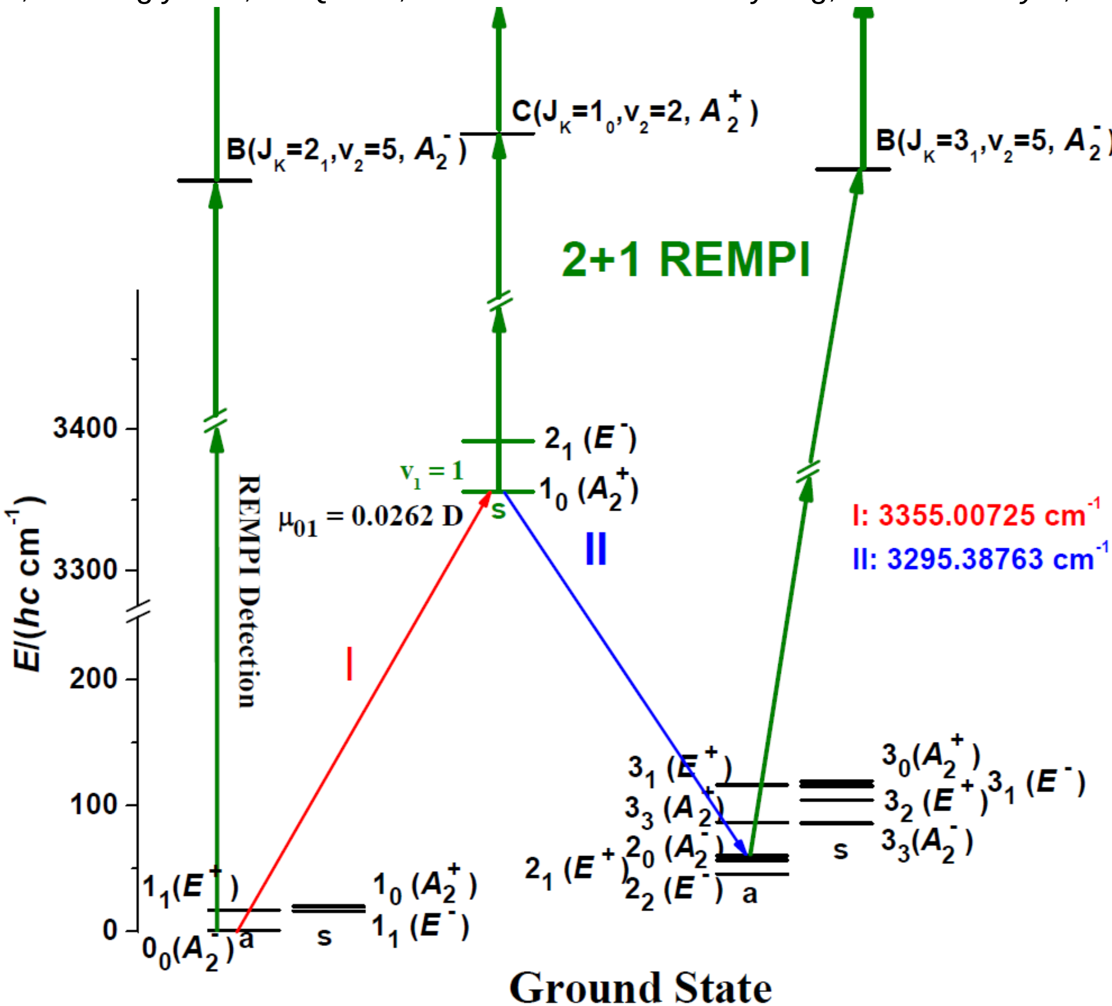
P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider and G. Seyfang, *J. Chem. Phys*., 143, 244305 (2015)



- Search for levels showing tunneling switching at 2400 cm^{-1} where parity (+, –) is defined (See also FE04)
- 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.

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

Conclusion

1,2-dithiine is a chiral molecule which may be a good candidate to measure the parity violating energy difference $\Delta_{pv}E$ between the enantiomers

Initial analyses of the high resolution GHz and THz spectra were successful

Acknowledgement

- The group of Martin Quack at ETH Zürich: www.ir.ETHz.ch
- Special thanks to Fabienne Arn and Guido Grassi for help in the synthesis work

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