ETH zürich

# A Combined Gigahertz and Terahertz (FTIR) Spectroscopic Investigation of Meta-D-phenol: Observation of Tunneling Switching

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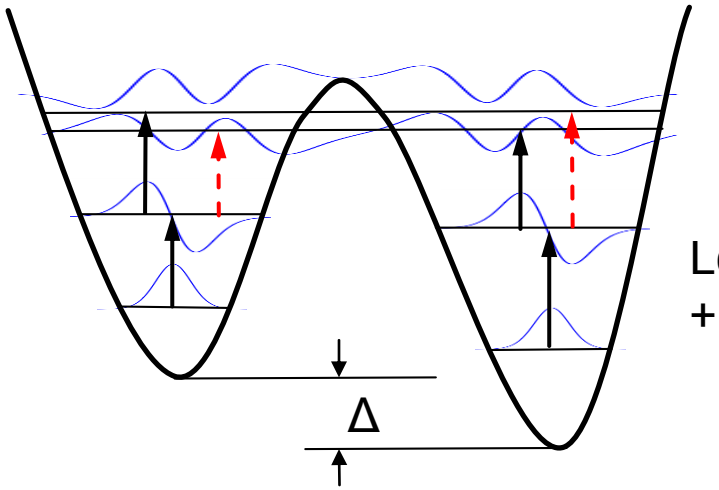
Tunneling switching in asymmetric potentials

Tunneling switching seen in small molecules so far
Here: a large molecule

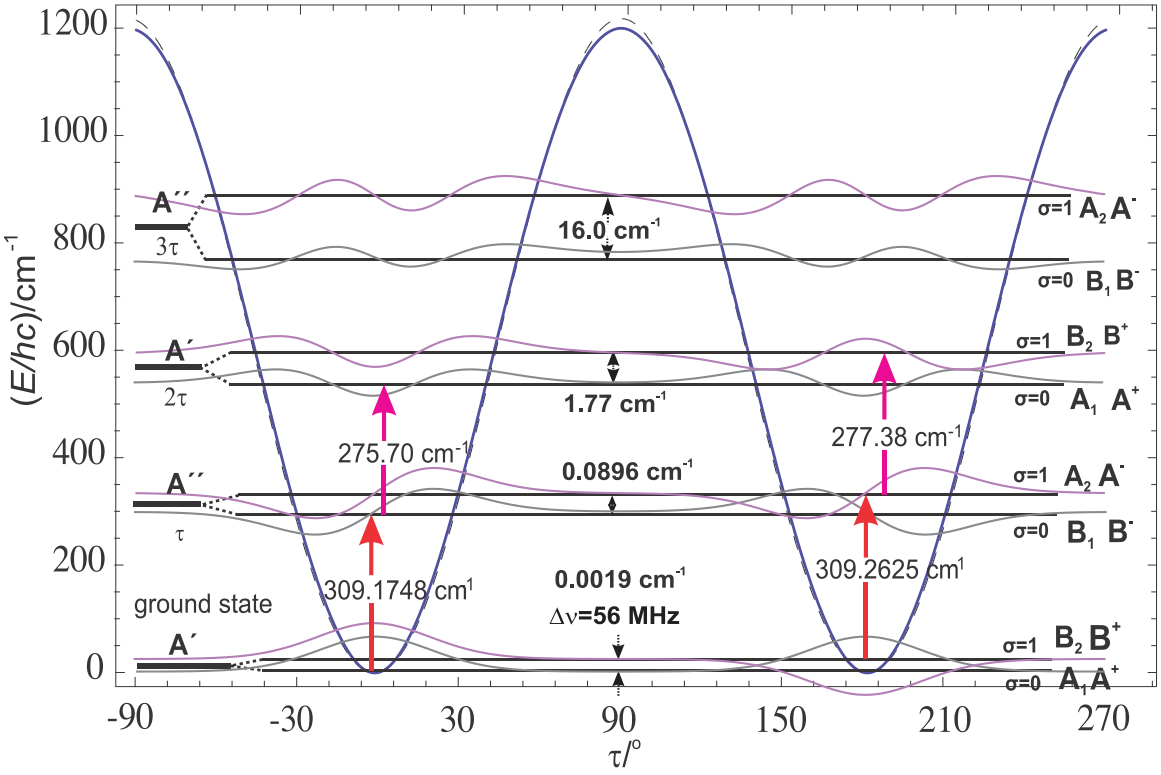


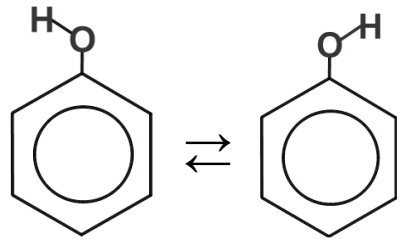

Delocalized wave functions
+ “forbidden transitions”

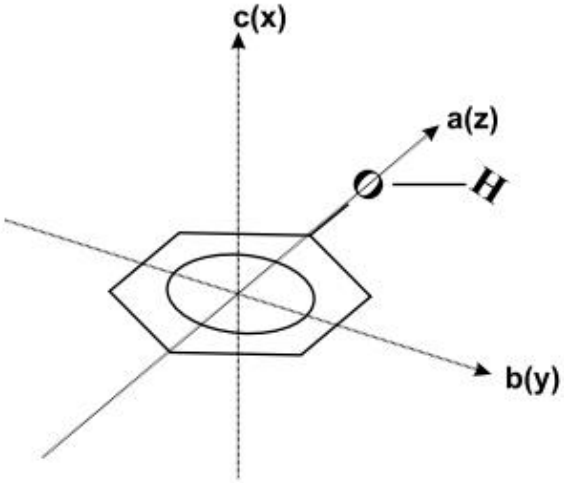
Localized wave functions
+ “Allowed transitions”

Why? Important for experiments on molecular parity violation, see also talk FA06

# -OH torsion in phenol : Tunneling



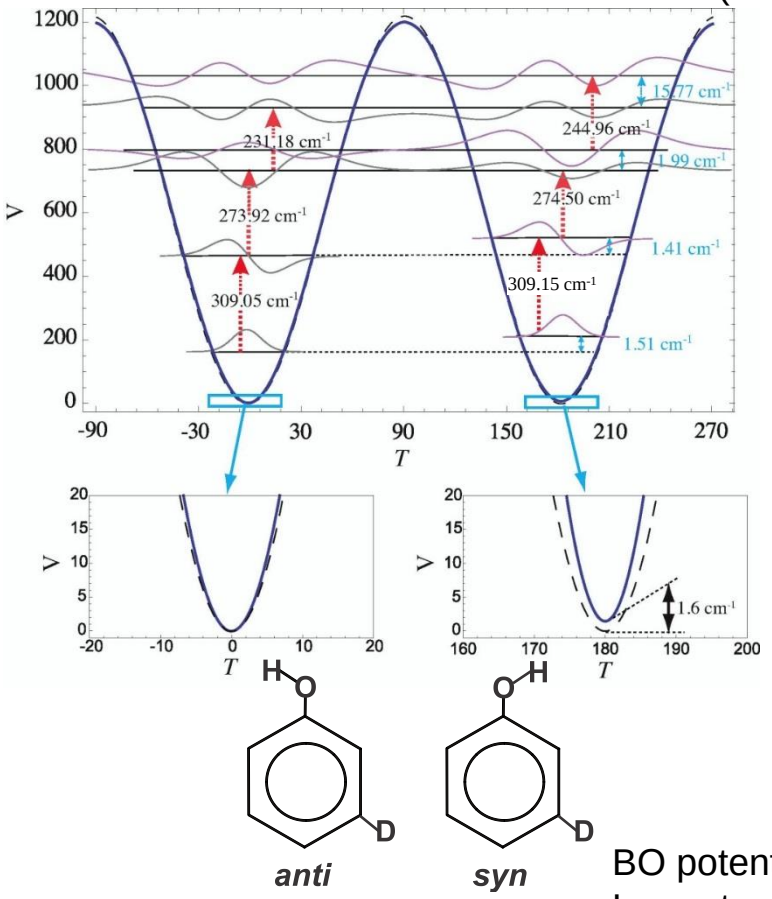


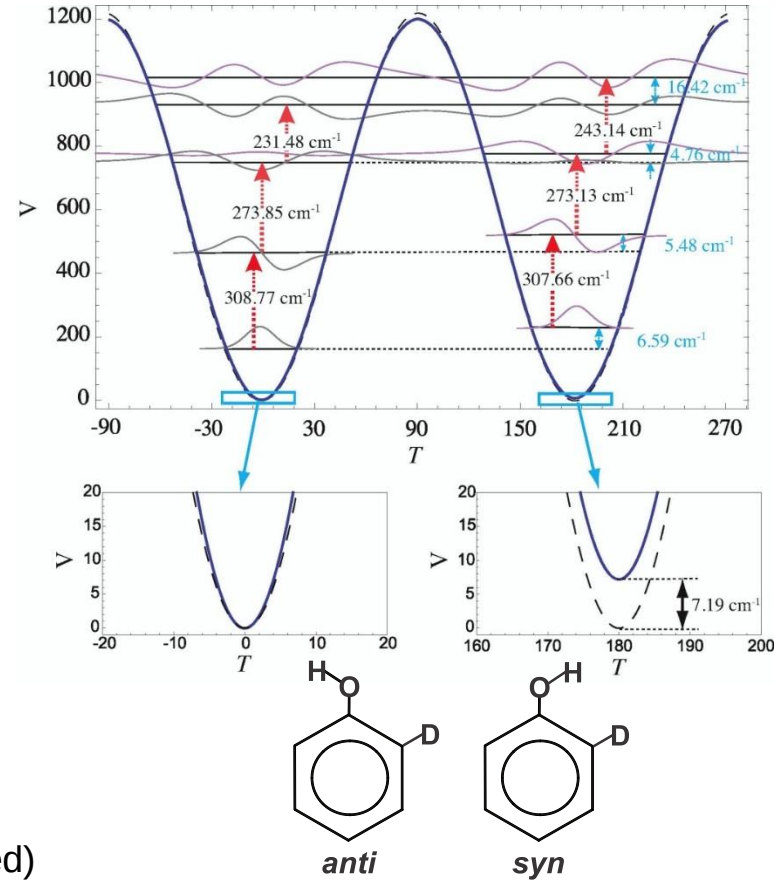
MW: E. Mathier, D. Welti, A. Bauder and Hs. H. Günthard, *J. Mol.Spectrosc.**37**,* 63-76 (1971)
C. Tanjaroon, S. G. Kukolich, *J. Phys.Chem.A* **113,** 9185-9192. (2009)
T. Pedersen, N. W. Larsen and L. Nygaard, *J. Mol. Struc.* **4**, 59 (1969)

IR: S. Albert, Ph. Lerch, R. Prentner and M. Quack, *Angew. Chem. Int. Ed.**52**,* 346-349 (2013)

# Introduction of an asymmetry in the effective potential (with symmetric Born-Oppenheimer potential) by zero point energy effects

Torsional potential of D-phenol predicted using the Quasiadiabatic Channel Reaction Path Hamiltonian (RPH) approach

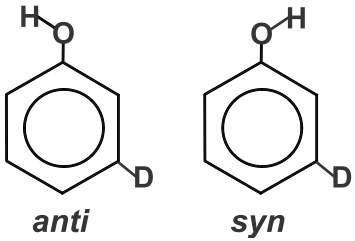


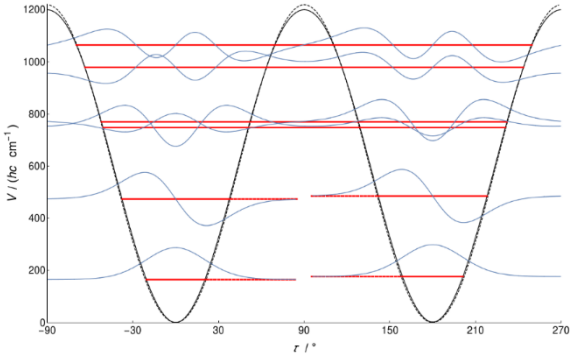




BO potential (dashed)
Lowest adiabatic channel potential (bold)

S. Albert, Ph. Lerch, R. Prentner and M. Quack, *Angew. Chem. Int. Ed.**52**,* 346-349 (2013)

# Aims




- To characterize the asymmetry in the effective –OH torsional potential energy function of D-phenol.
- Rotational and vibrational levels to be probed through high resolution GHz and THz spectra.
- Important goal is to observe and understand the tunneling switching dynamics in the higher excited states as prototypical case also for asymmetry due to parity violation in chiral molecules.

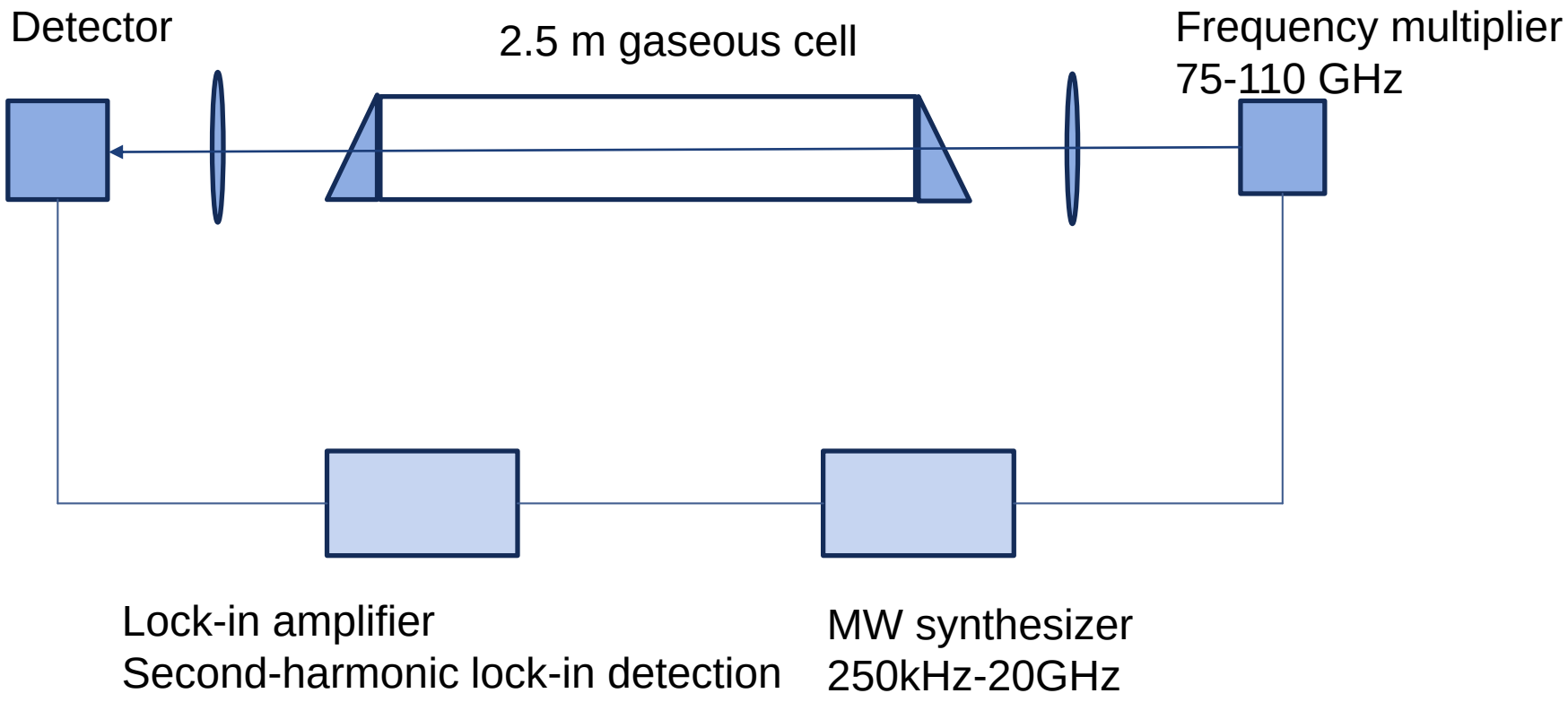
Theory (current version as used here):

B. Fehrensen, D. Luckhaus and M. Quack, *Chem. Phys. Lett.* **300**, 312 (1999), *Chem. Phys.* **338**, 90 (2007)
R. Prentner, M. Quack, J. Stohner and M. Willeke, *J. Phys. Chem. A* **119**, 12805 (2015)

Historic background on the quasiadiabatic channel reaction path Hamiltonian approach:

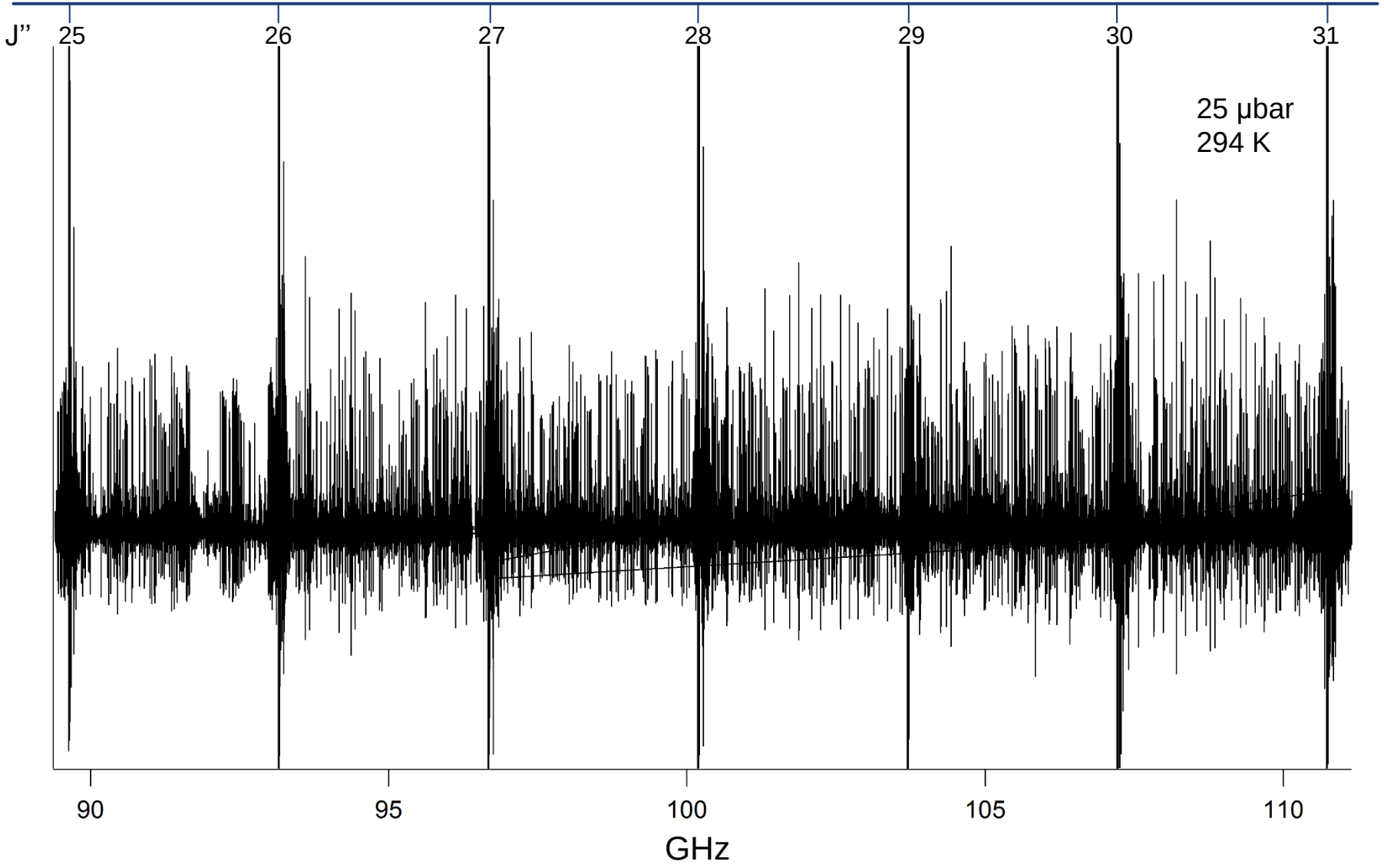
L. Hofacker, *Z. Naturforsch.A* **18**, 607 (1963)
R. A. Marcus, *J. Chem. Phys.* **43**, 1598 (1965)
J. T. Hougen, P.R. Bunker and J.W.C. Johns, *J. Mol. Spectrosc.* **34**, 136 (1970)
M. Quack and J. Troe, *Ber. Bunsenges. Phys.Chem.* **78**, 240 (1974)
W. H. Miller, N.C. Handy and J.E. Adams, *J. Phys.Chem,* **72**, 99 (1980)

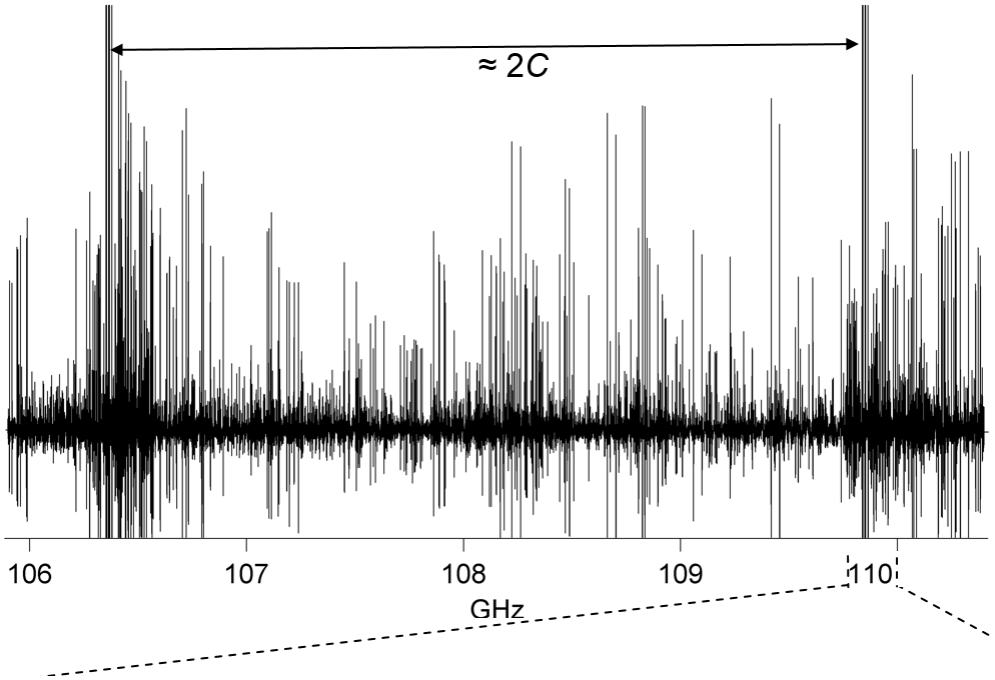
# GHz setup at ETH Zürich

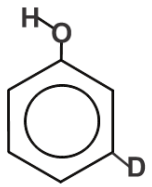



M. Suter and M. Quack, *Appl. Opt.* **54**, 4417-4431 (2015)

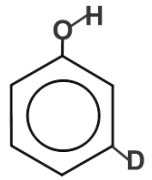
# Overview spectra: 90-110 GHz





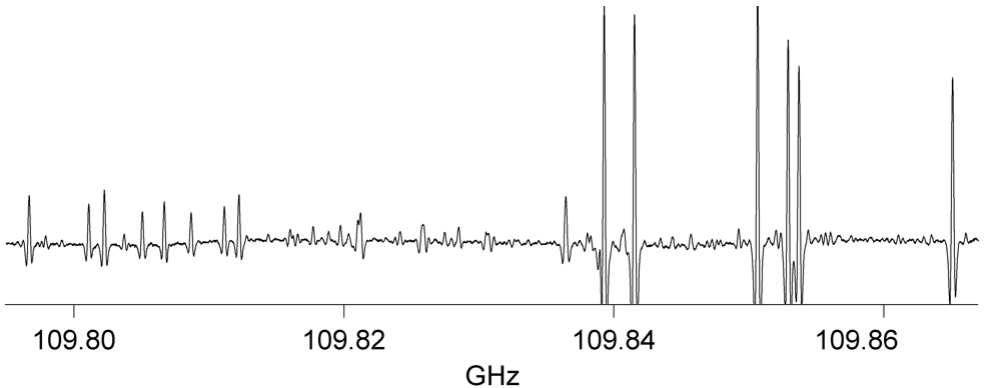




*anti*

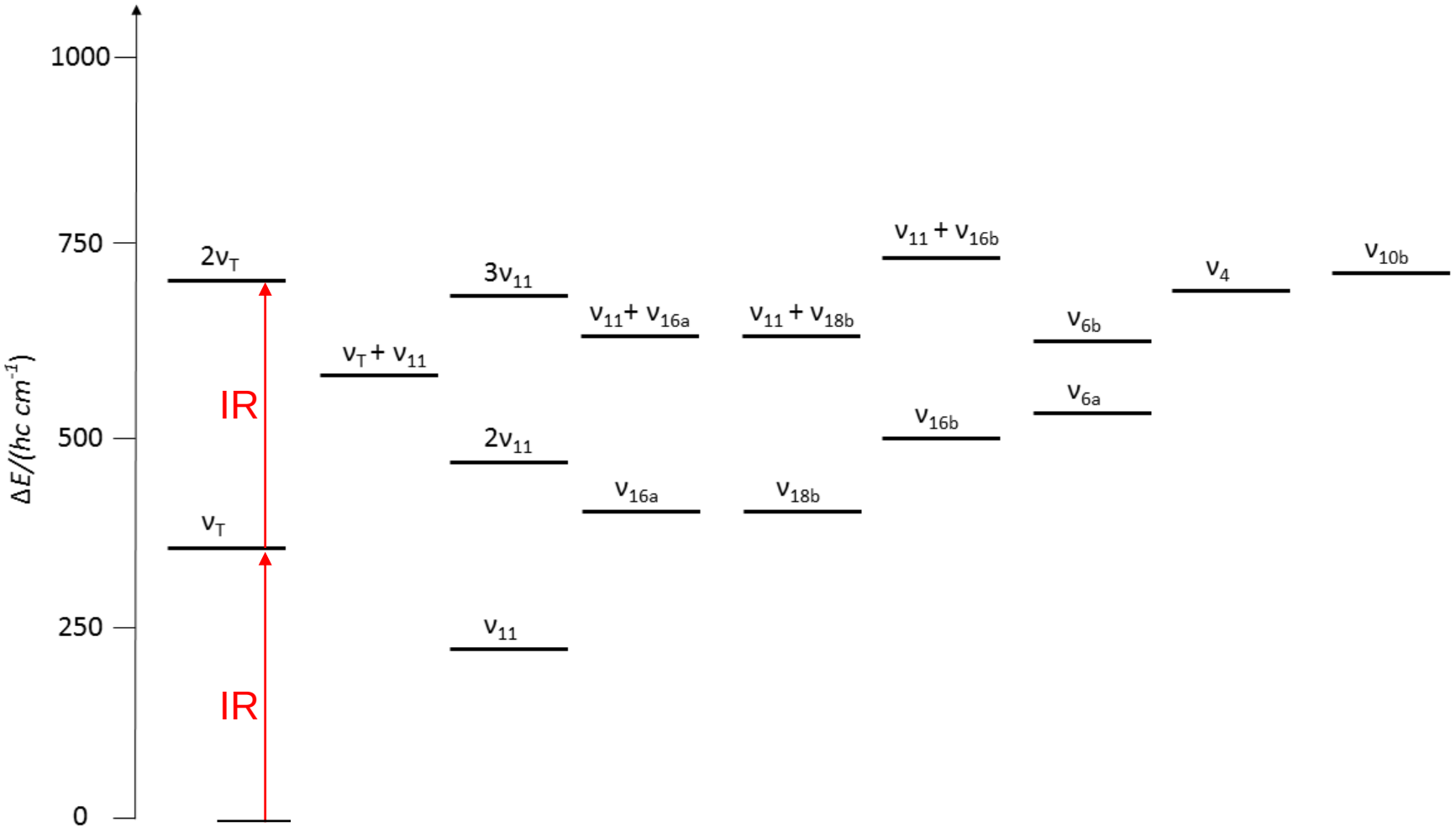



*syn*

FWHM ≈ 200 kHz

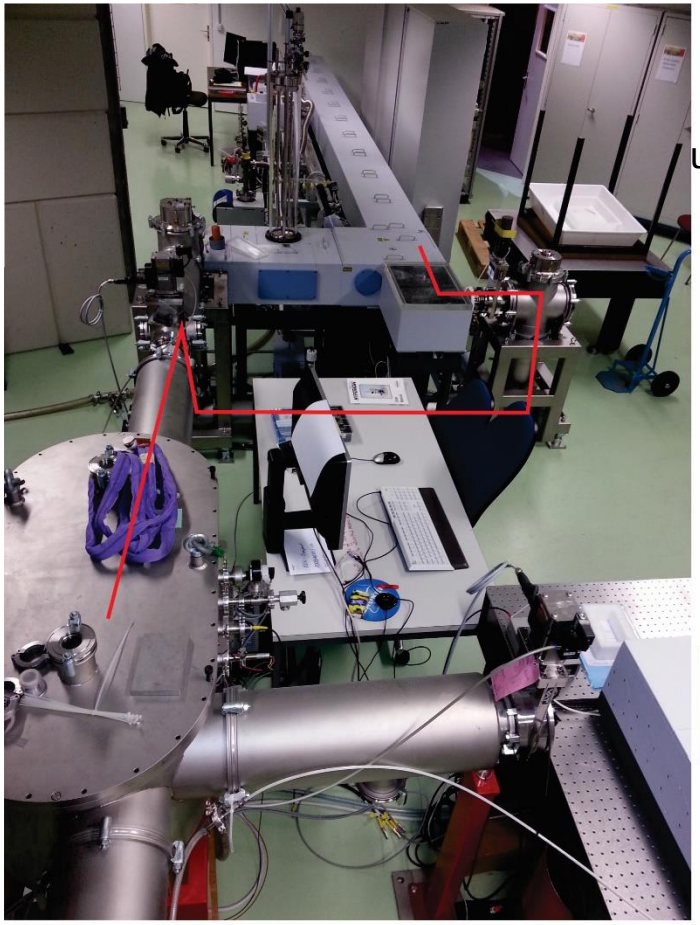


# All low energy levels in m-D-phenol

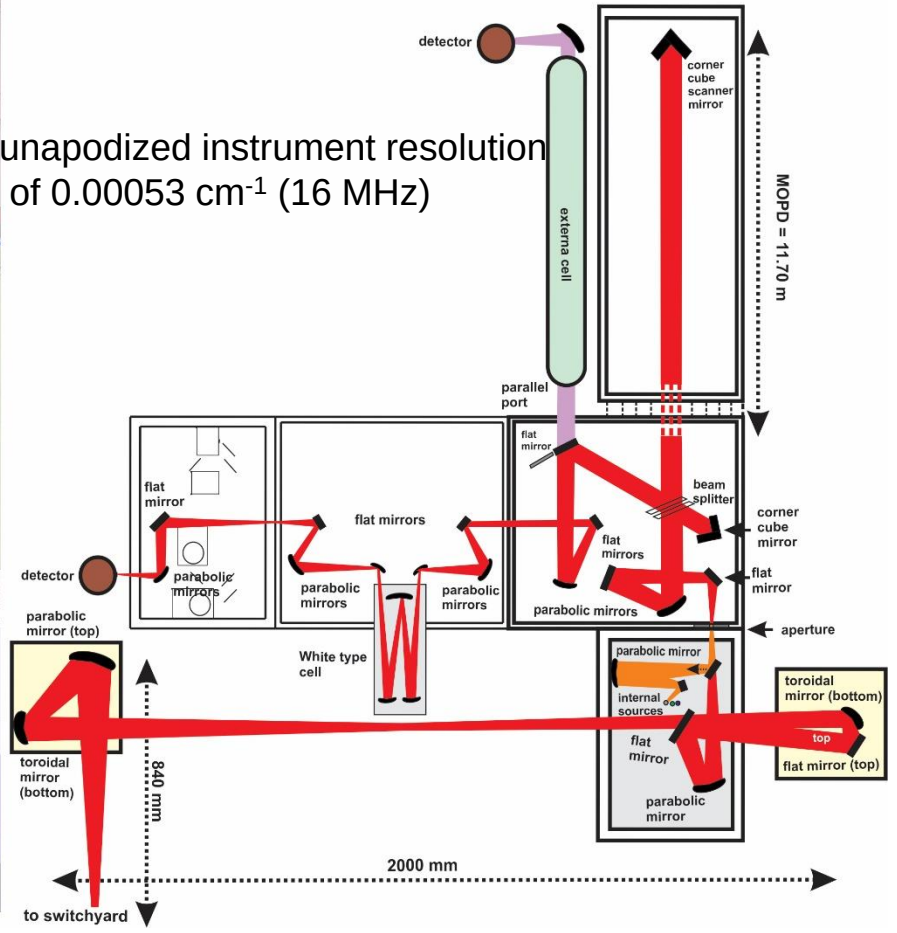



harmonic frequencies calculated at B3LYP/cc-pVTZ level

# Synchrotron-based high resolution FTIR setup at the Swiss Light Source

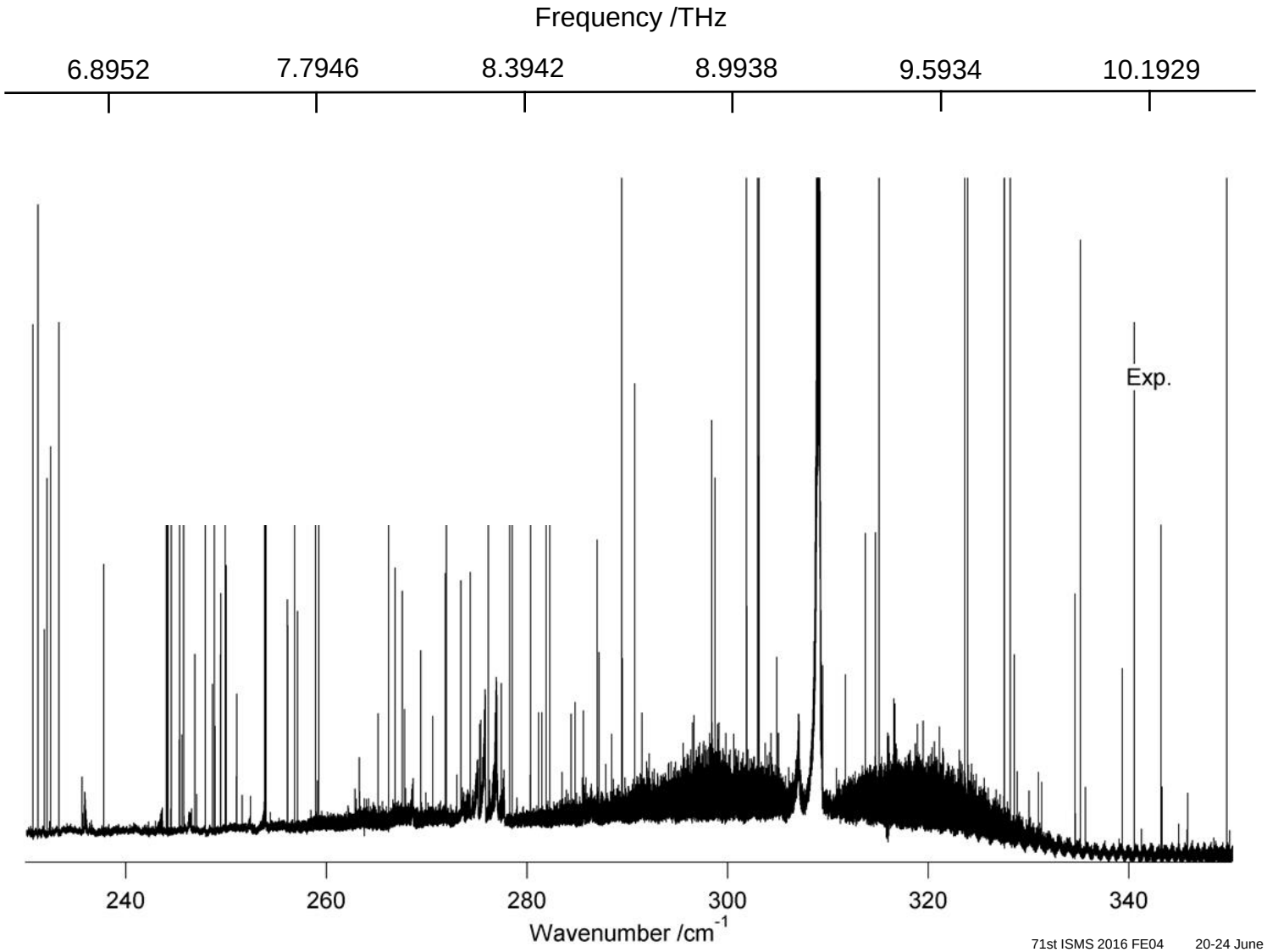


unapodized instrument resolution of 0.00053 $cm^{-1}$ (16 MHz)

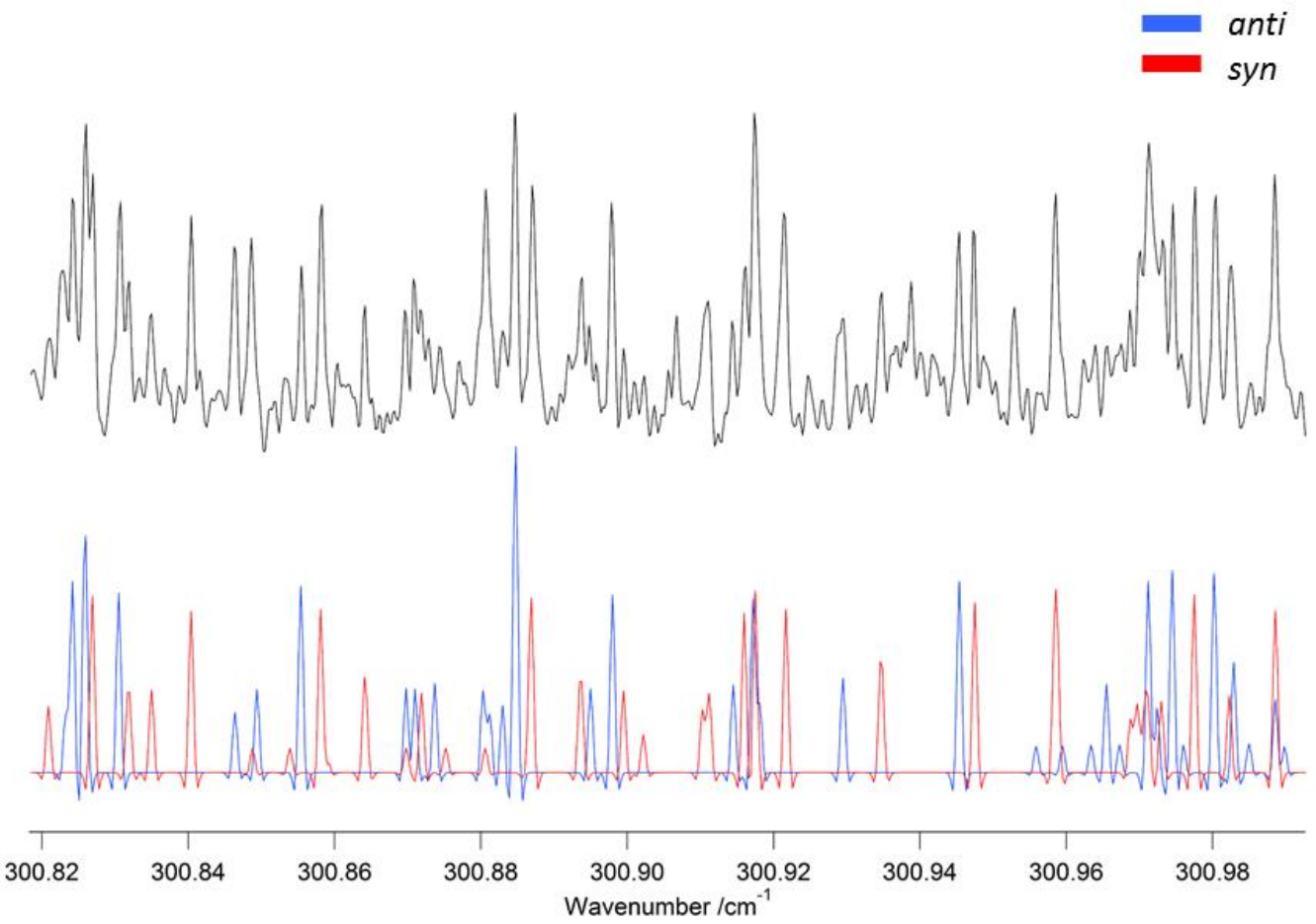



S. Albert, K.K. Albert, Ph. Lerch, M. Quack, *Faraday Discussions*, **150**, 71-99 (2011)
S. Albert, K. K. Albert and M. Quack, *High Resolution Fourier Transform Infrared Spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 2 (Eds. M. Quack and F. Merkt), John Wiley & Sons, Ltd, Chichester,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

# Overview spectra: 230-360 $cm^{-1}$ (6.895-10.793 THz)

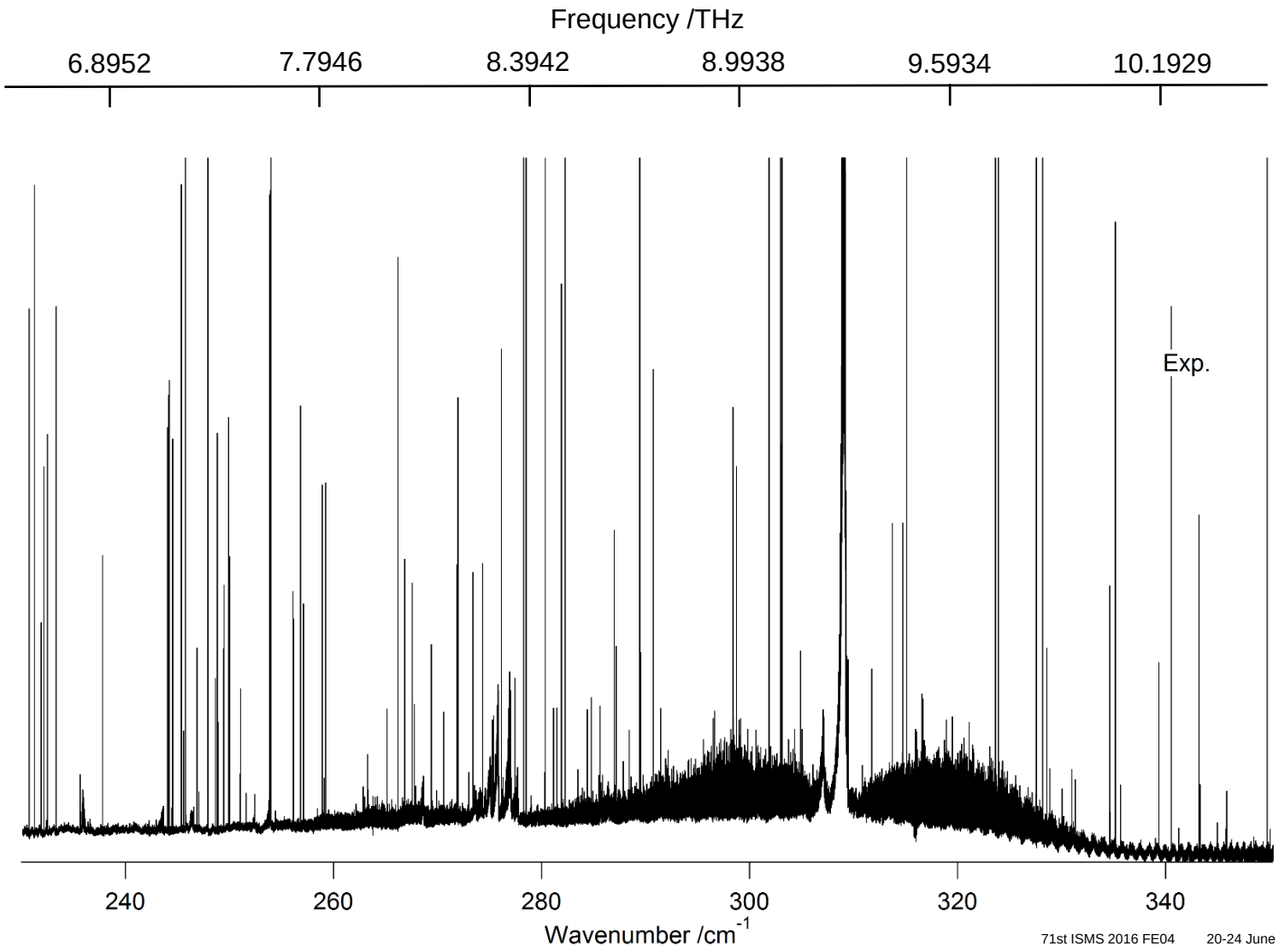


# Torsional fundamental

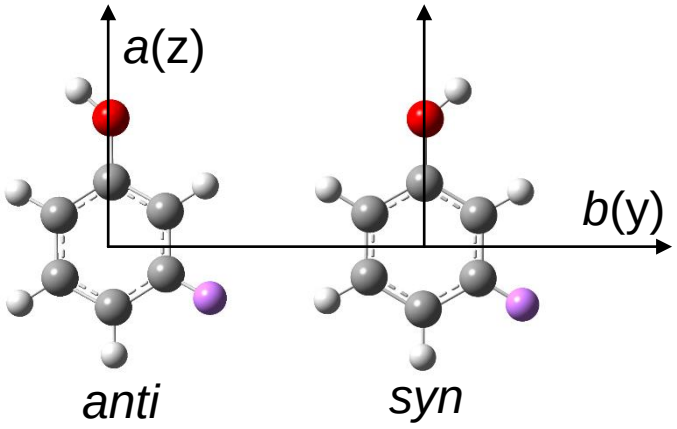


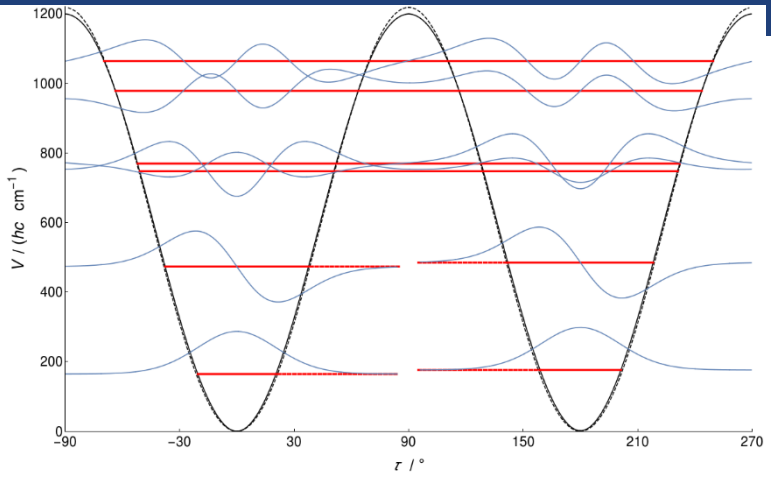

No signs of perturbations

# Overview spectra: 230-360 cm$^{-1}$ (6.895-10.793 THz)



# Possible perturbations?




| $C_s$ | $E$ | $\sigma_h$ | | |
|---|---|---|---|---|
| $A'$ | 1 | 1 | $x, y, R_z$ | $x^2, y^2, z^2, xy$ |
| $A''$ | 1 | −1 | $z, R_x, R_y$ | $yz, xz$ |

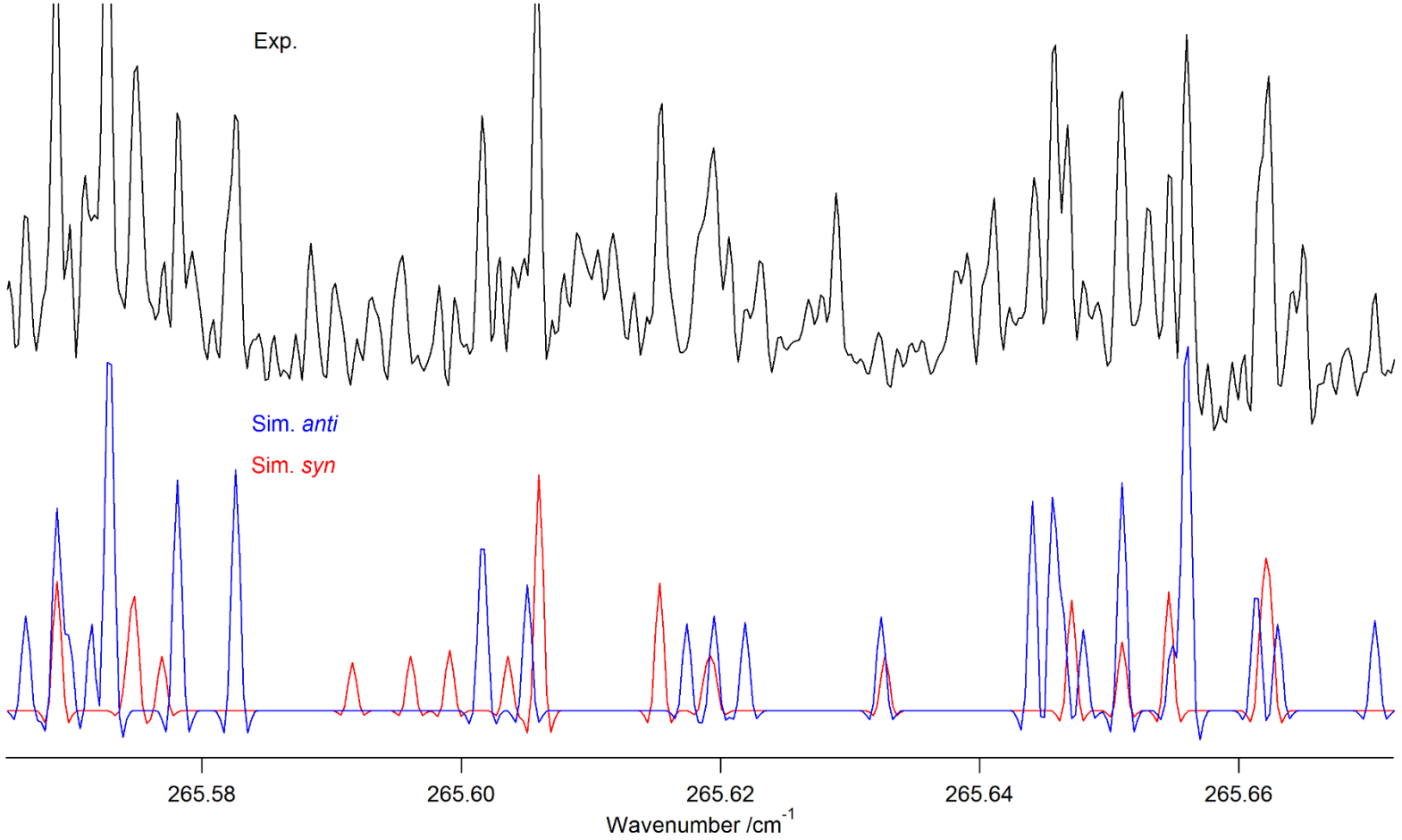
For two states with the different symmetries:

Coriolis couplings along the *a*- or *b*-axis

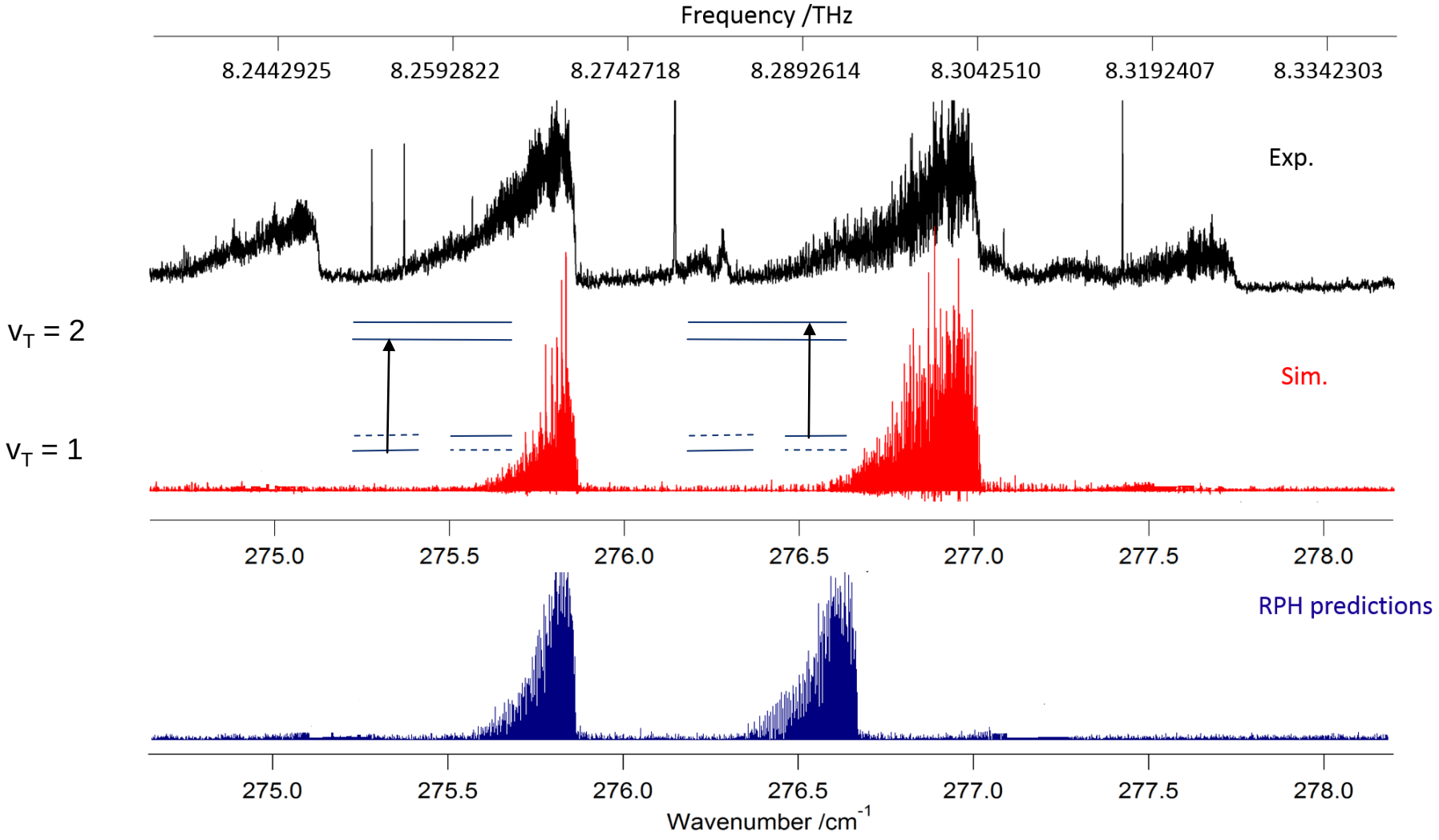
For two states with the same symmetry:

Coriolis couplings along the *c*-axis or anharmonic resonance

# First torsional hot band



# First torsional hot band :observation and assignment of tunneling-rotation-vibration transitions



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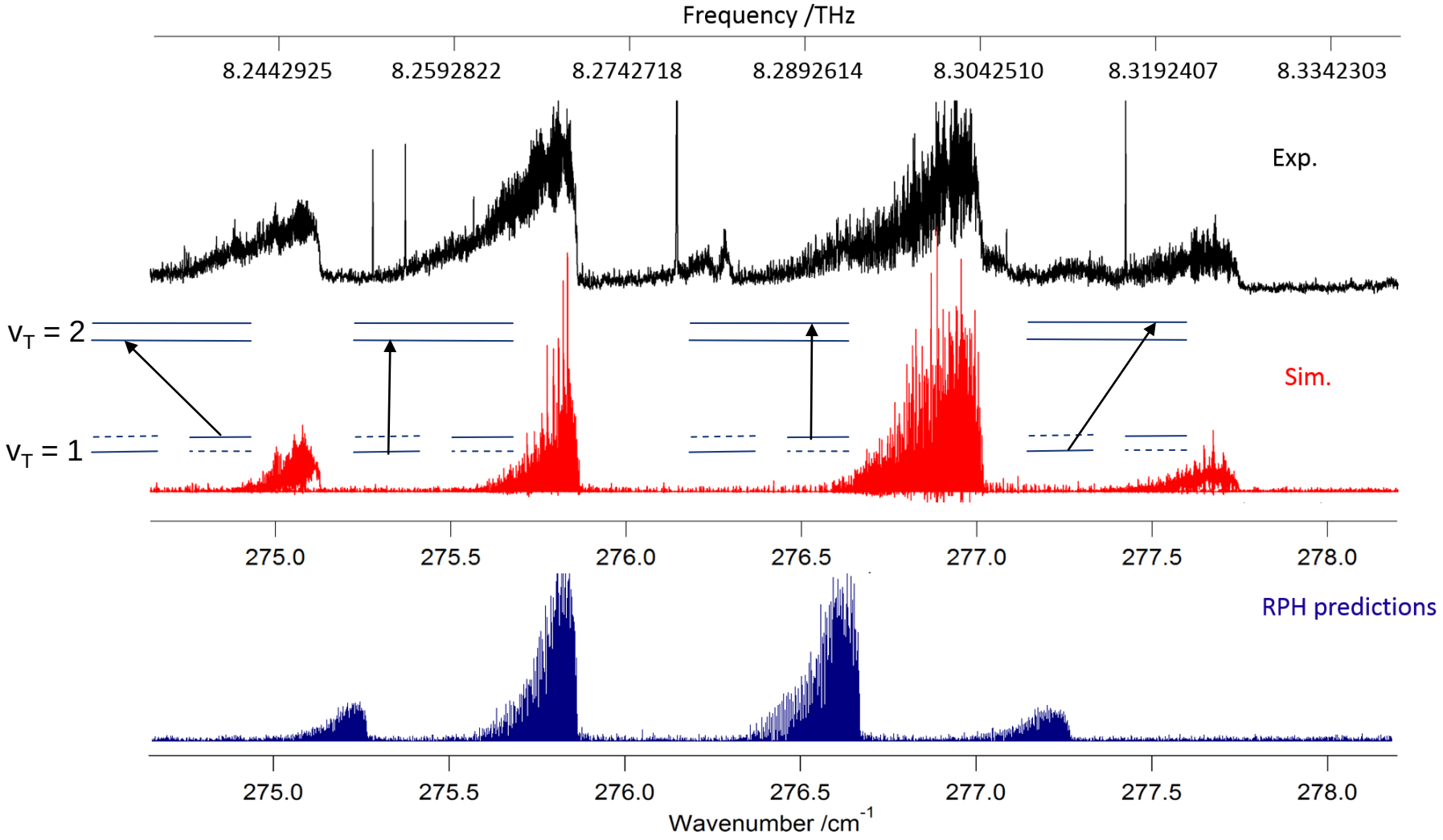
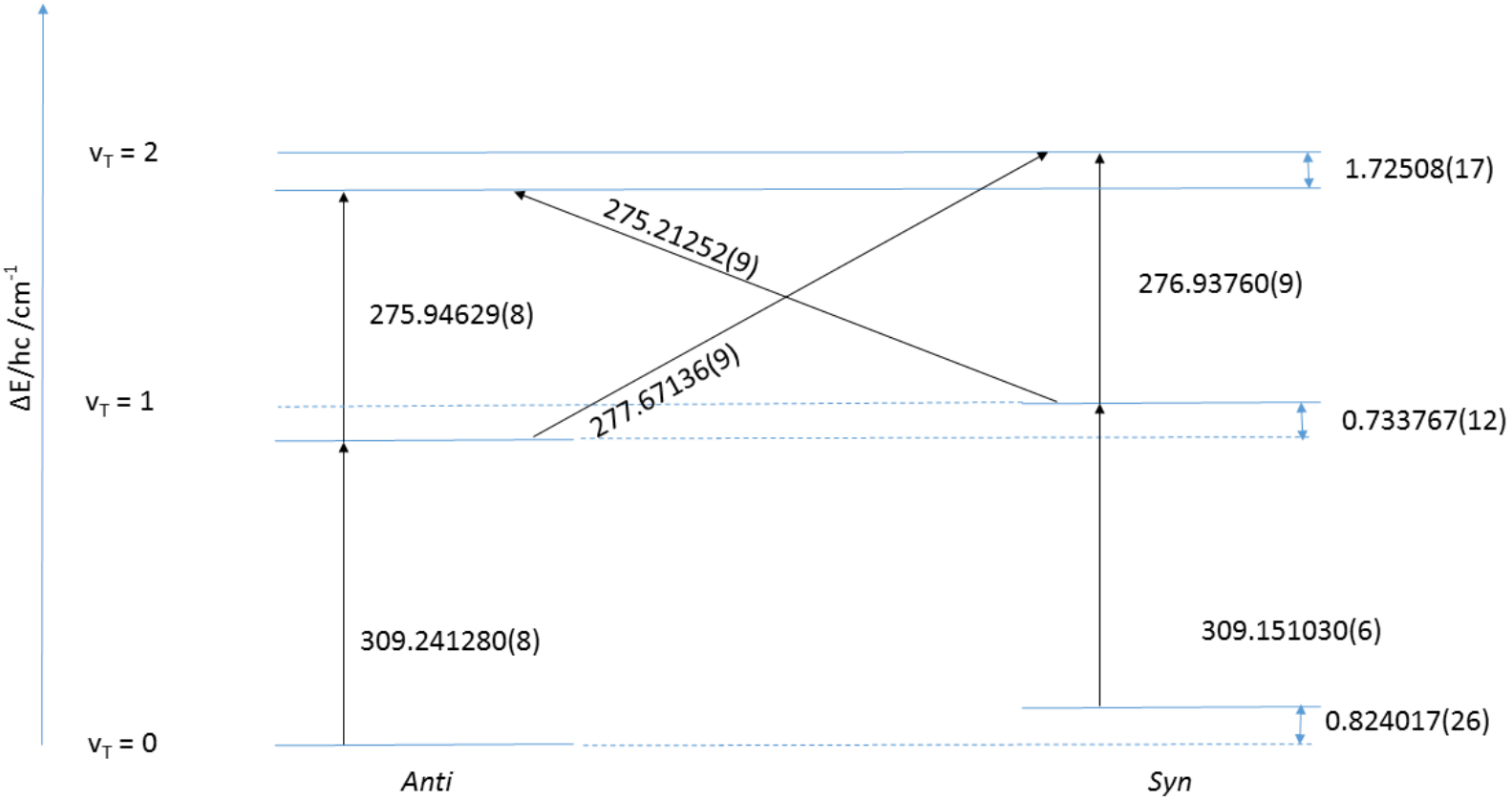
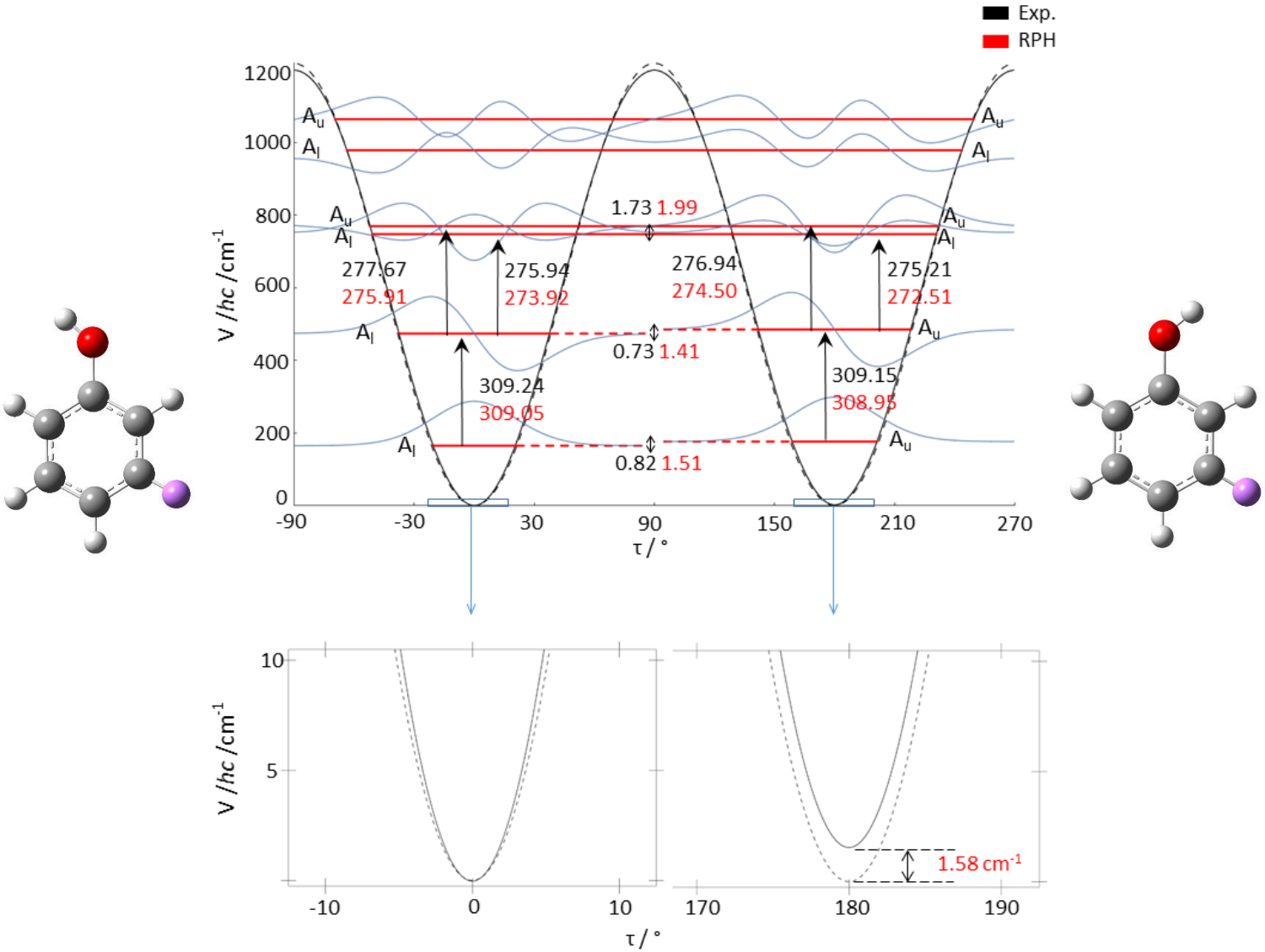


# Energy level scheme of the torsional polyad in m-D-phenol



# The torsional polyad in m-D-phenol: Tunneling switching



# Conclusion

Tunneling switching finally observed in m-D-phenol spectra!

## Acknowledgement


- The group of Martin Quack at ETH Zürich: www.ir.ETHz.ch
- Special thanks to Daniel Zindel for the synthesis work

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