ETH zürich

A Combined Gigahertz and Terahertz Synchrotron-based Fourier Transform Infrared Spectroscopic Investigation of Ortho-D-phenol: Tunneling Switching

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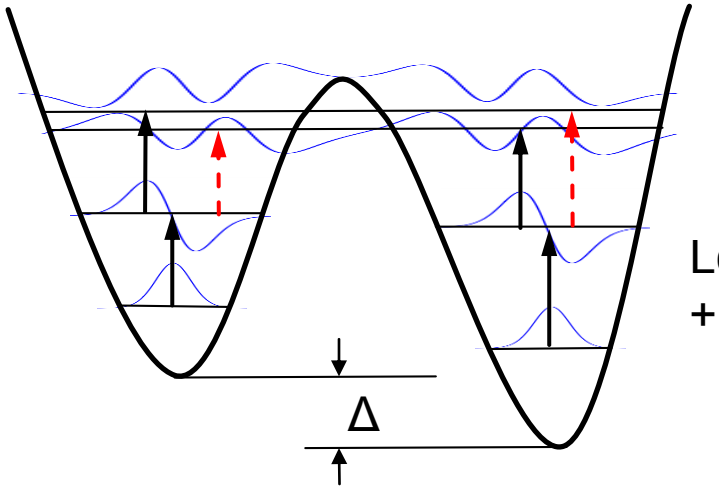
Tunneling switching in asymmetric potentials

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

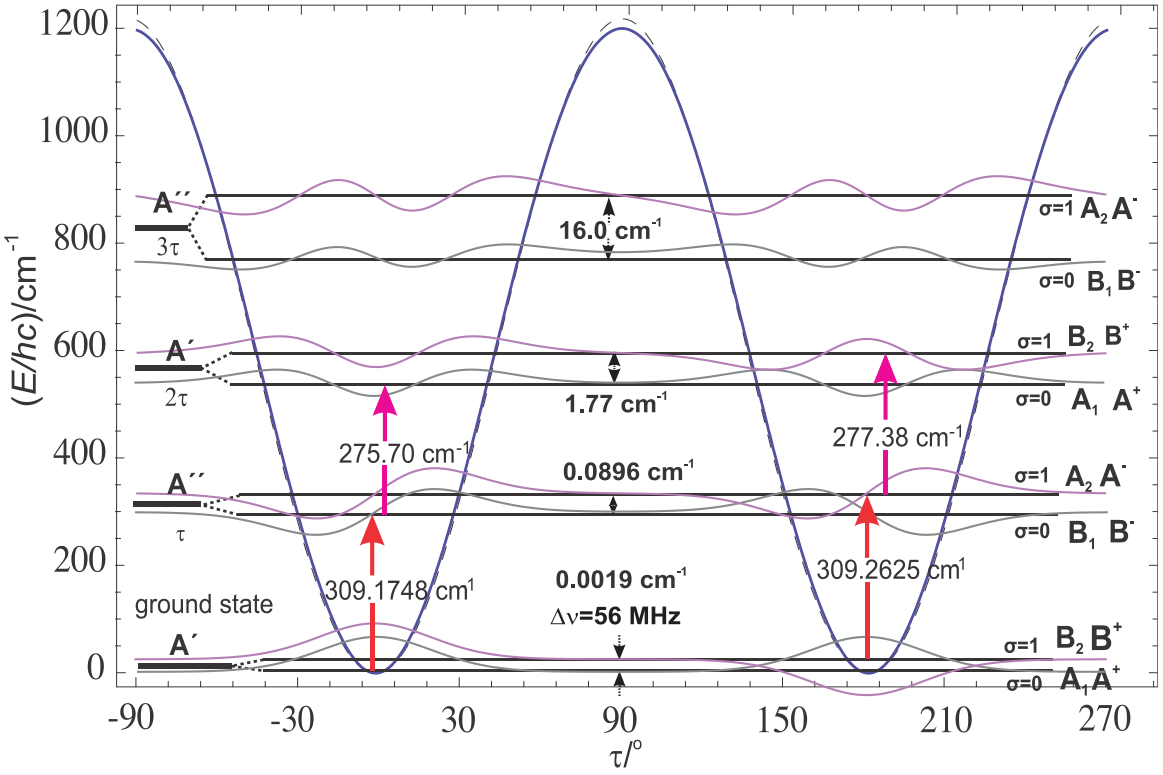


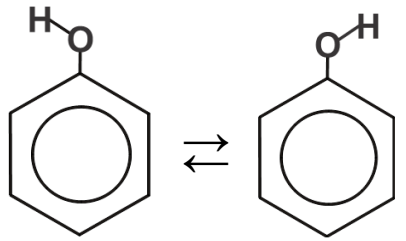
Delocalized wave functions
+ “forbidden transitions”

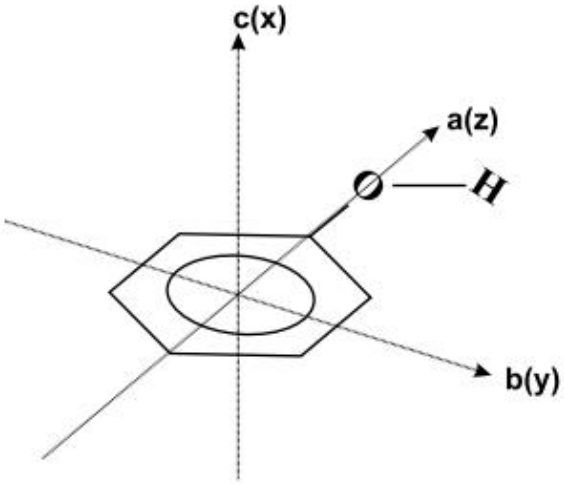
Localized wave functions
+ “Allowed transitions”

Why? Important for experiments on molecular parity violation, see also talk WG11

-OH torsion in phenol : Tunneling





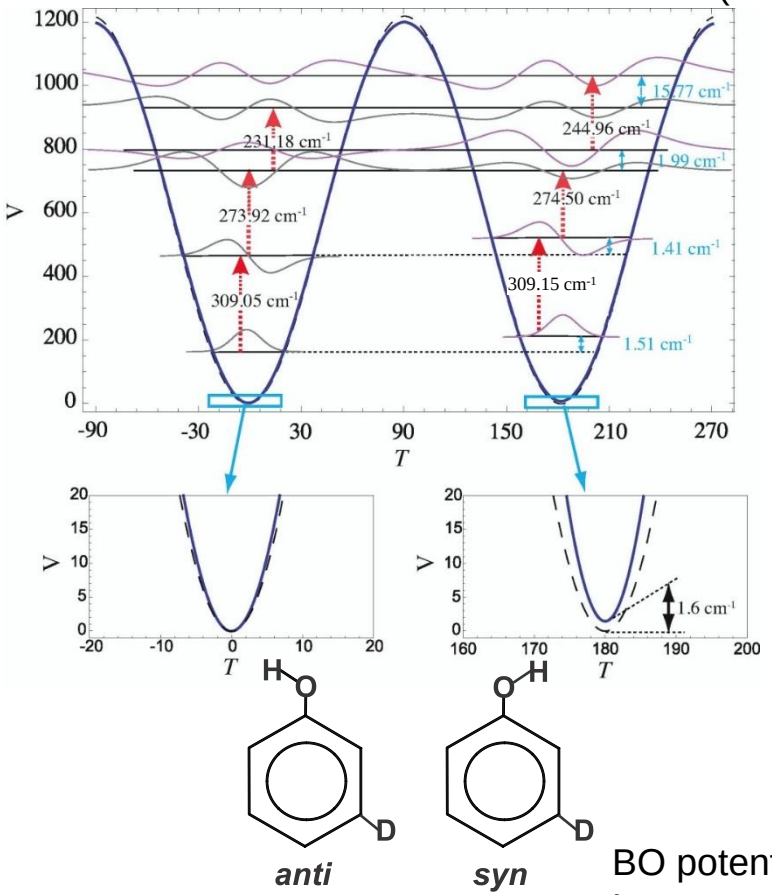


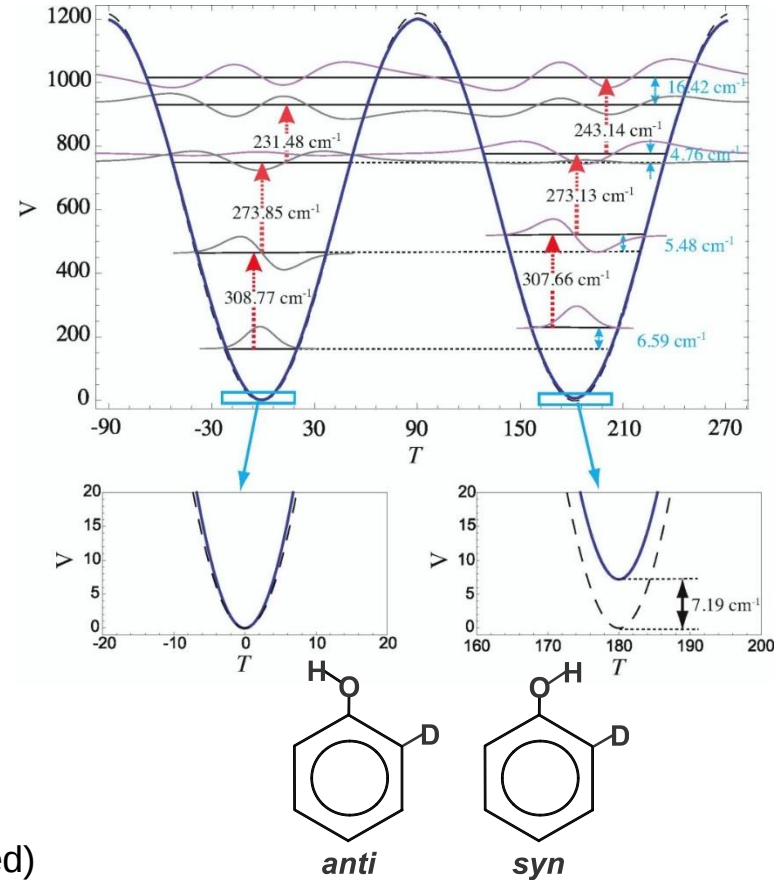
MW: E. Mathier, D. Welti, A. Bauder and Hs. H. Günthard, *J. Mol.Spectrosc.**37**,* 63-76 (1971)
C. Tanjaroon, S. G. Kukolich, *J. Phys.Chem.A* **113,** 9185-9192. (2009)
T. Pedersen, N. W. Larsen and L. Nygaard, *J. Mol. Struc.* **4**, 59 (1969)

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

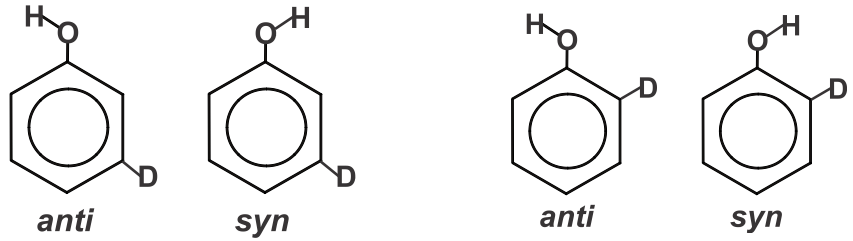


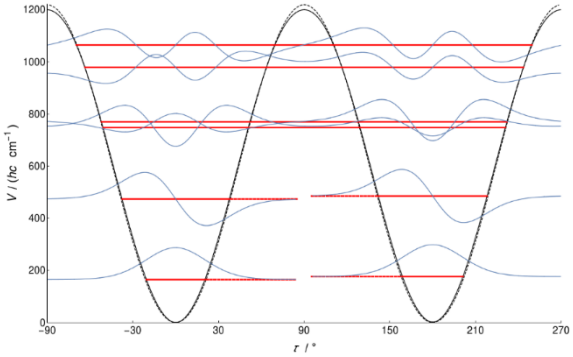


BO potential (dashed)
Lowest adiabatic channel potential (bold)

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-phenols.
- 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.

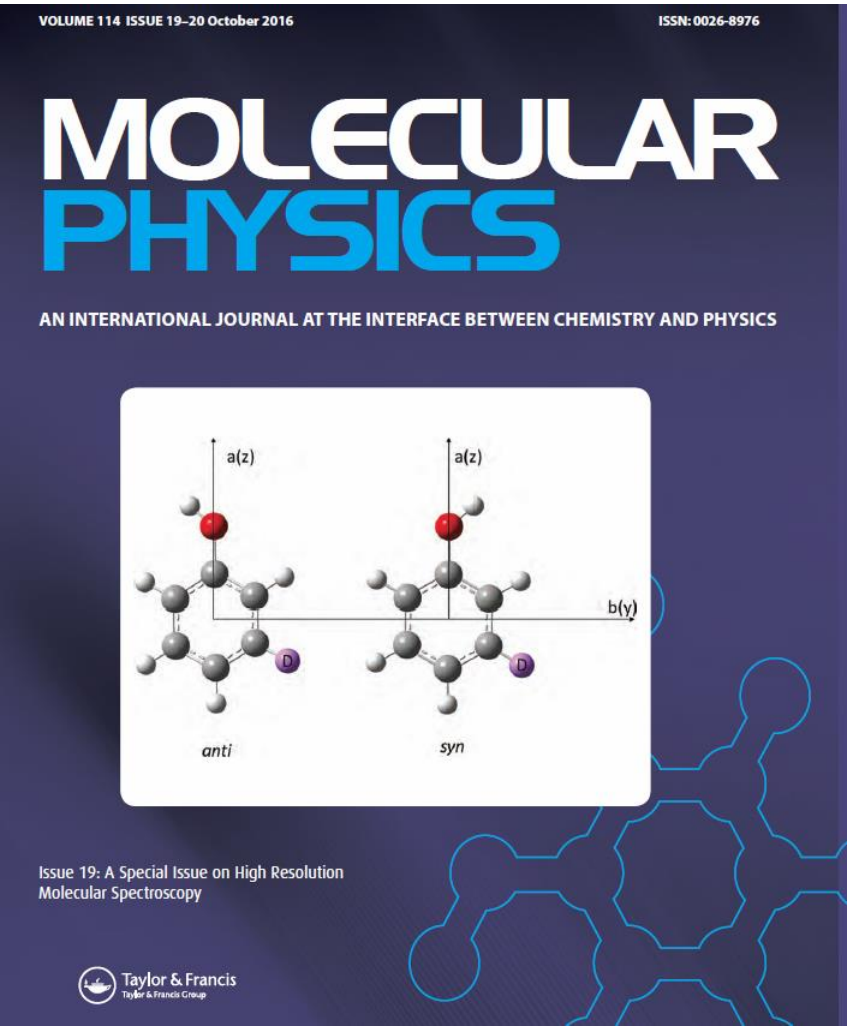
Theory:

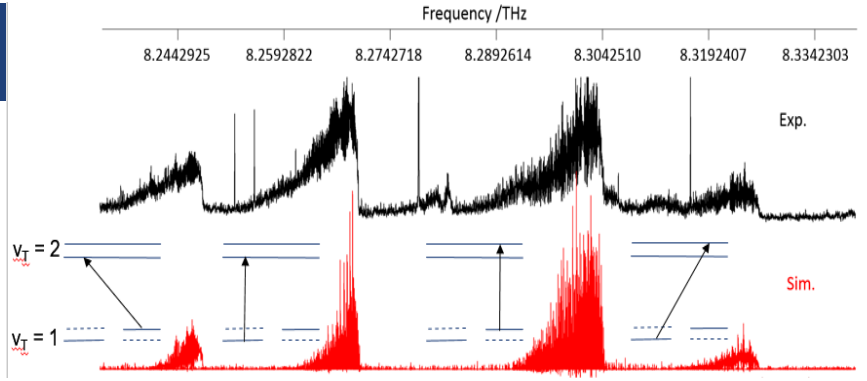
B. Fehrensen, D. Luckhaus and M. Quack, *Chem. Phys. Lett.* **300**, 312 (1999), *Chem. Phys.* **338**, 90 (2007)
R. Prentner, M. Quack, J. Stohner and M. Willeke, *J. Phys. Chem. A* **119**, 12805 (2015)

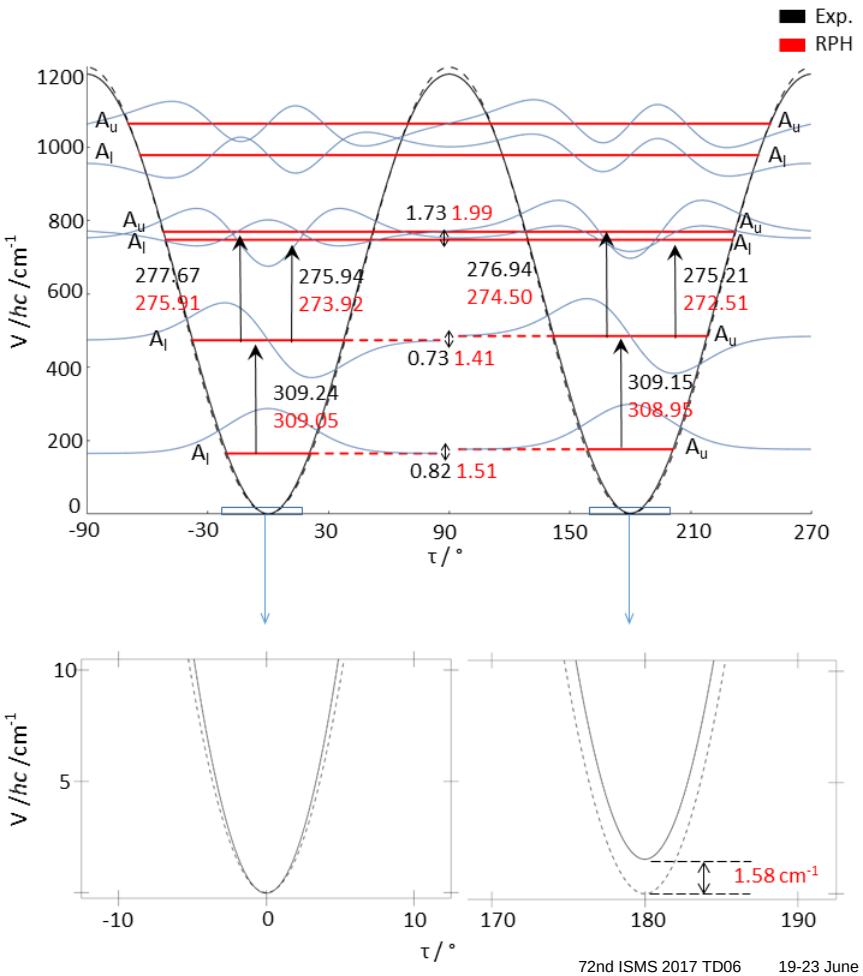
Theoretical background on the quasiadiabatic channel reaction path Hamiltonian approach:

H.W. Miller, N.C. Handy and J.E. Adams, *J. Phys.Chem,* **72**, 99 (1980)
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)

Tunneling Switching in m-D-phenol

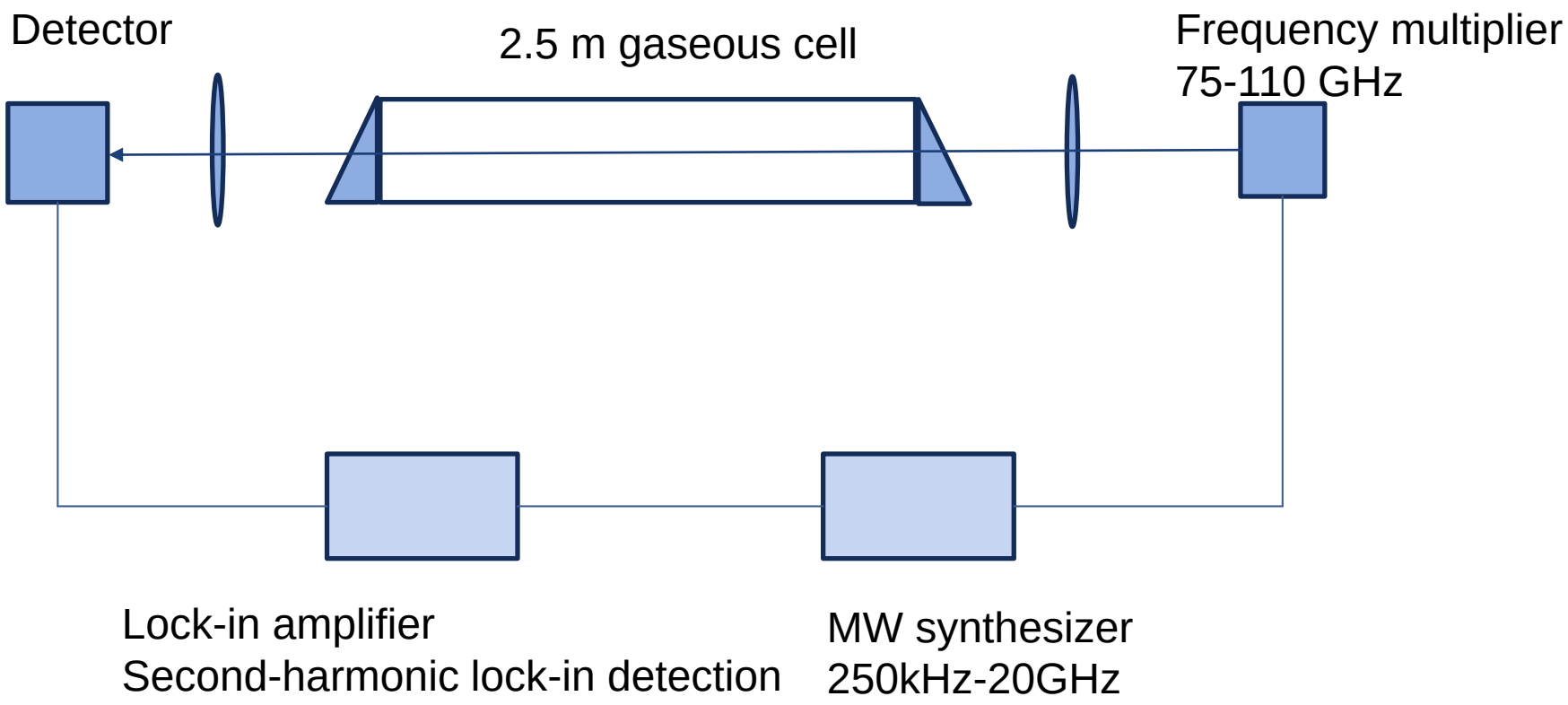






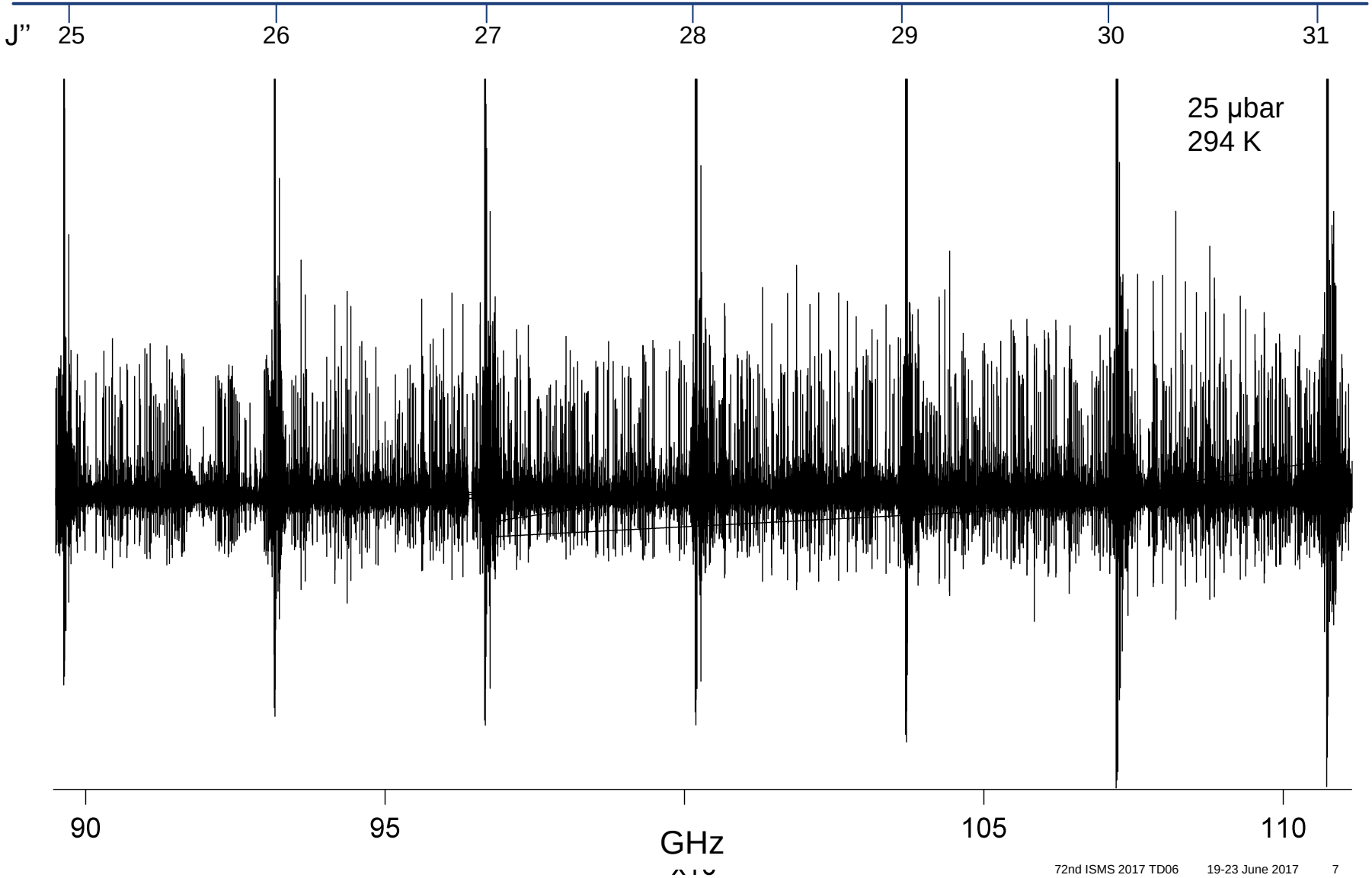
S. Albert, Z. Chen, C. Fábri, P. Lerch, R. Prentner and M. Quack, *Mol.Phys.*, **114**, 2751-2768 (2016).

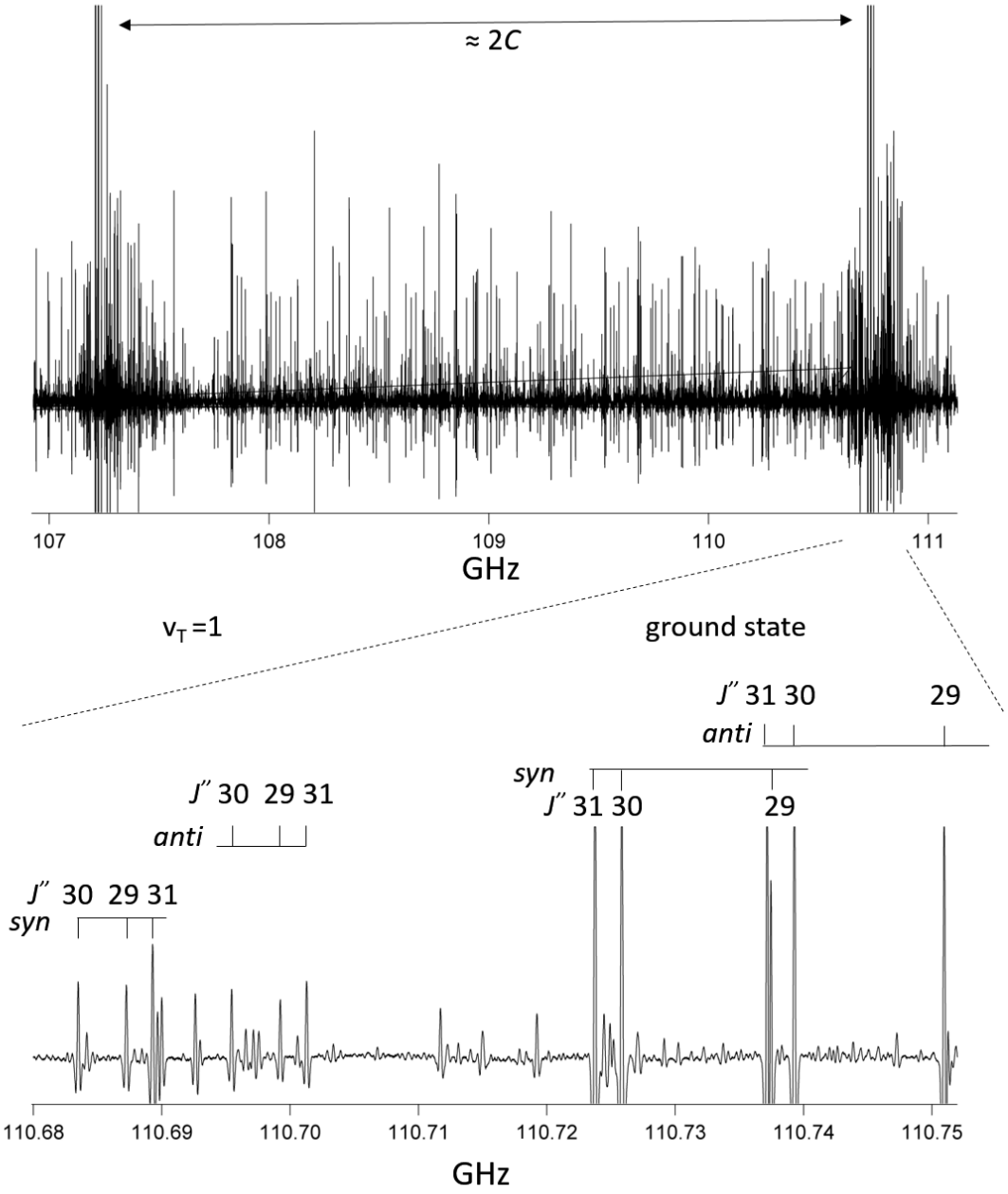
GHz setup at ETH Zürich

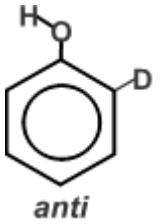


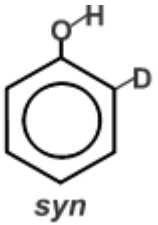
M. Suter and M. Quack, *Appl. Opt.* **54**, 4417-4431 (2015)

Overview spectra: 90-110 GHz




≈ 2C
107
108
109
110
111
GHz
v_T =1
ground state
J″ 31 30
29
anti
syn
J″ 30 29 31
anti
J″ 31 30
29
syn
J″ 30 29 31
syn
110.68
110.69
110.70
110.71
110.72
110.73
110.74
110.75
GHz


H
O
D
anti


O
H
D
syn

FWHM ≈ 200 kHz

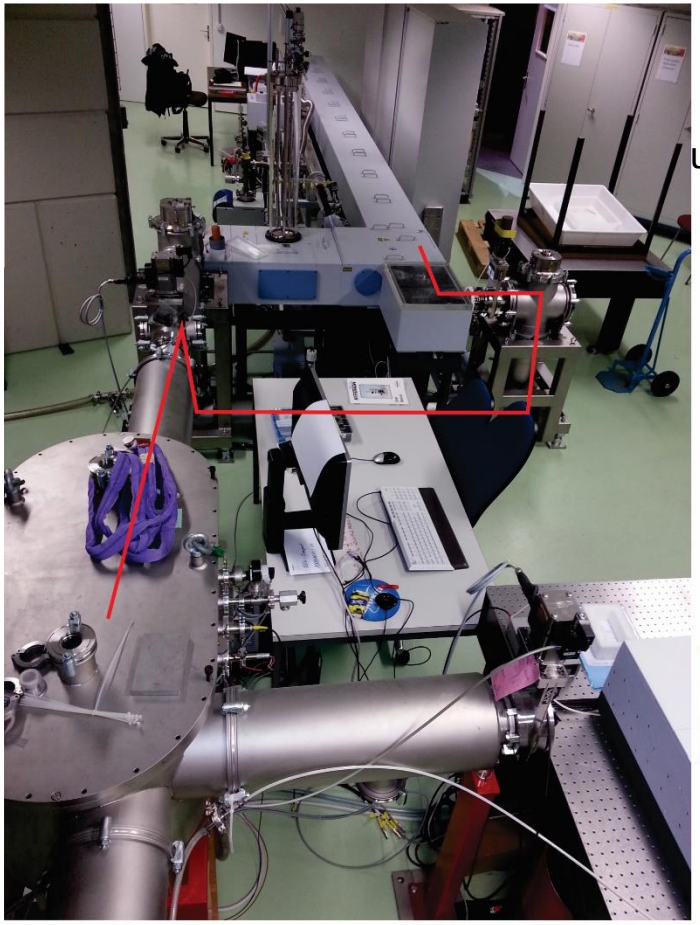
Spectroscopic parameters of the ground state and the first excited torsional state of o-D-Phenol (GHz study)

Watson's A-reduction, I^r-representation

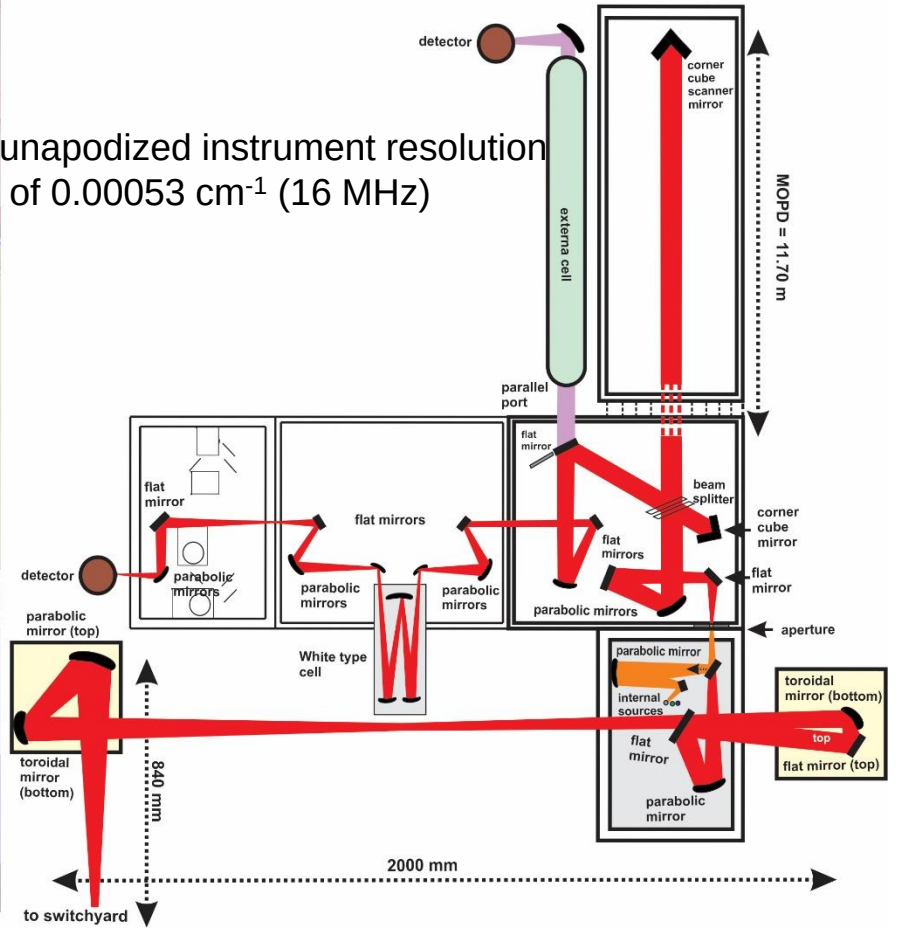
	Anti		*Syn*	
	v=0	v_T =1 (308.36 cm^{-1})	v=0	v_T =1 (307.94 cm^{-1})
Rotational constants / MHz				
A	5379.92505(12)	5379.029(22)	5375.84938(12)	5375.190(43)
B	2610.460600(81)	2605.6888(39)	2610.941439(84)	2606.1770(66)
C	1757.819470(81)	1757.31360(53)	1757.606533(86)	1757.12376(63)
Centrifugal distortion constants / kHz				
Δ_J	0.129920(56)	0.13010(31)	0.129881(60)	0.13032(36)
Δ_K	0.72780(26)	0.540(45)	0.72703(27)	0.39(13)
Δ_{JK}	0.18579(10)	0.18579[1]	0.18435(10)	0.39(13)
δ_j	0.043637(15)	0.043637	0.043643(16)	0.043643
δ_k	0.33381(12)	0.33381	0.33291(13)	0.33291
d_{rms} / kHz	13.08	22.74	13.52	25.88
No. of transitions	487	71	490	66

[1]Values without parenthesis held fixed to the respective values of the v = 0.

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

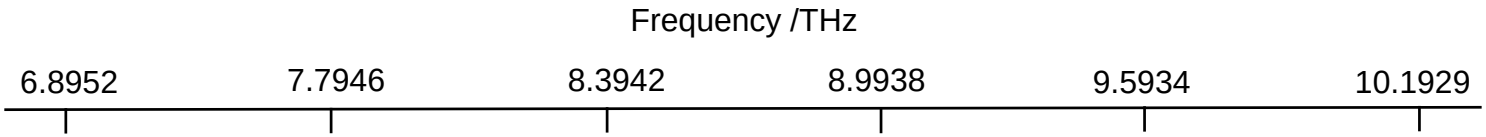


unapodized instrument resolution of 0.00053 cm^{-1} (16 MHz)

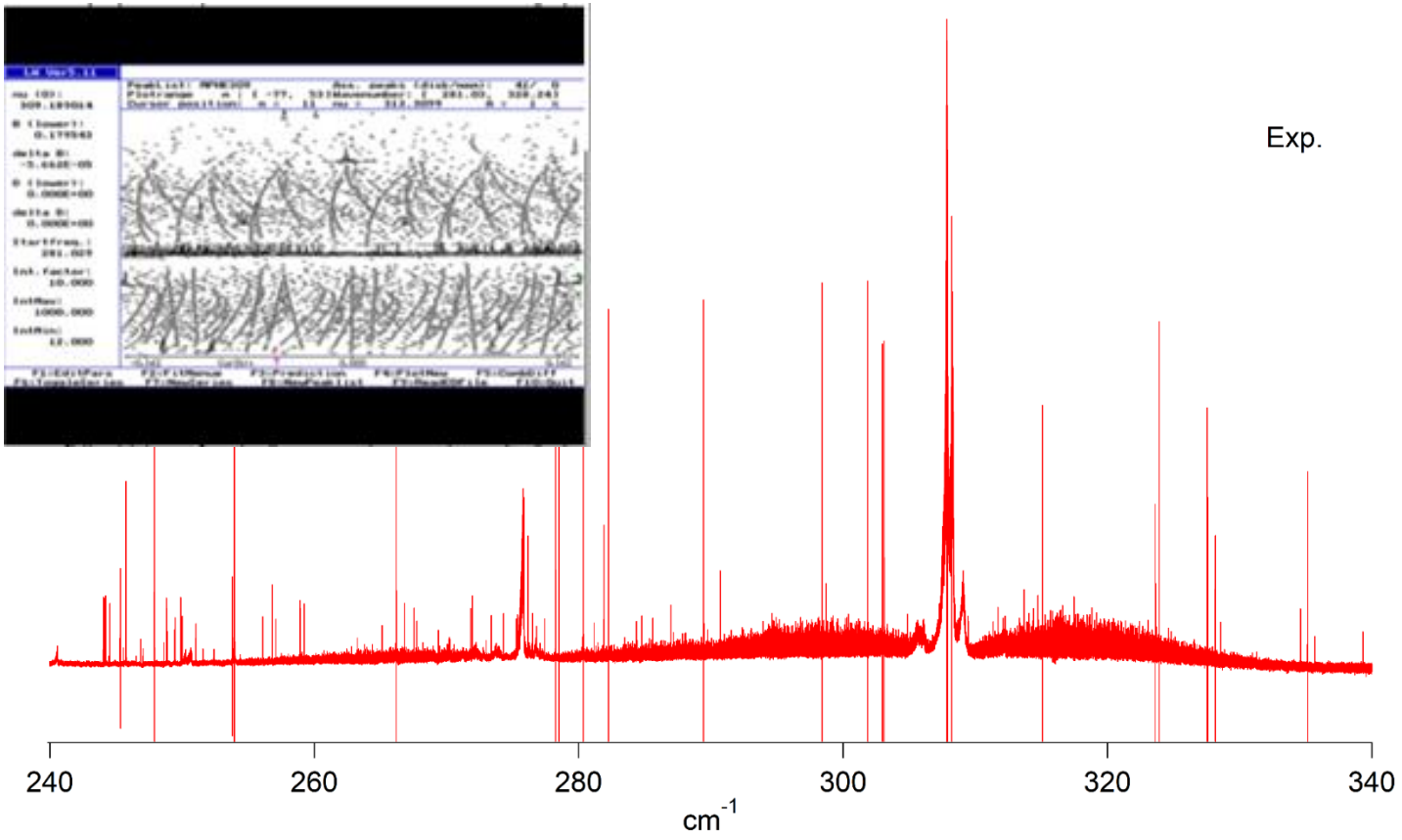


S. Albert, K.K. Albert, Ph. Lerch, M. Quack, *Faraday Discussions*, **150**, 71-99 (2011)
S. Albert, K. K. Albert and M. Quack, *High Resolution Fourier Transform Infrared Spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 2 (Eds. M. Quack and F. Merkt), John Wiley & Sons, Ltd, Chichester,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

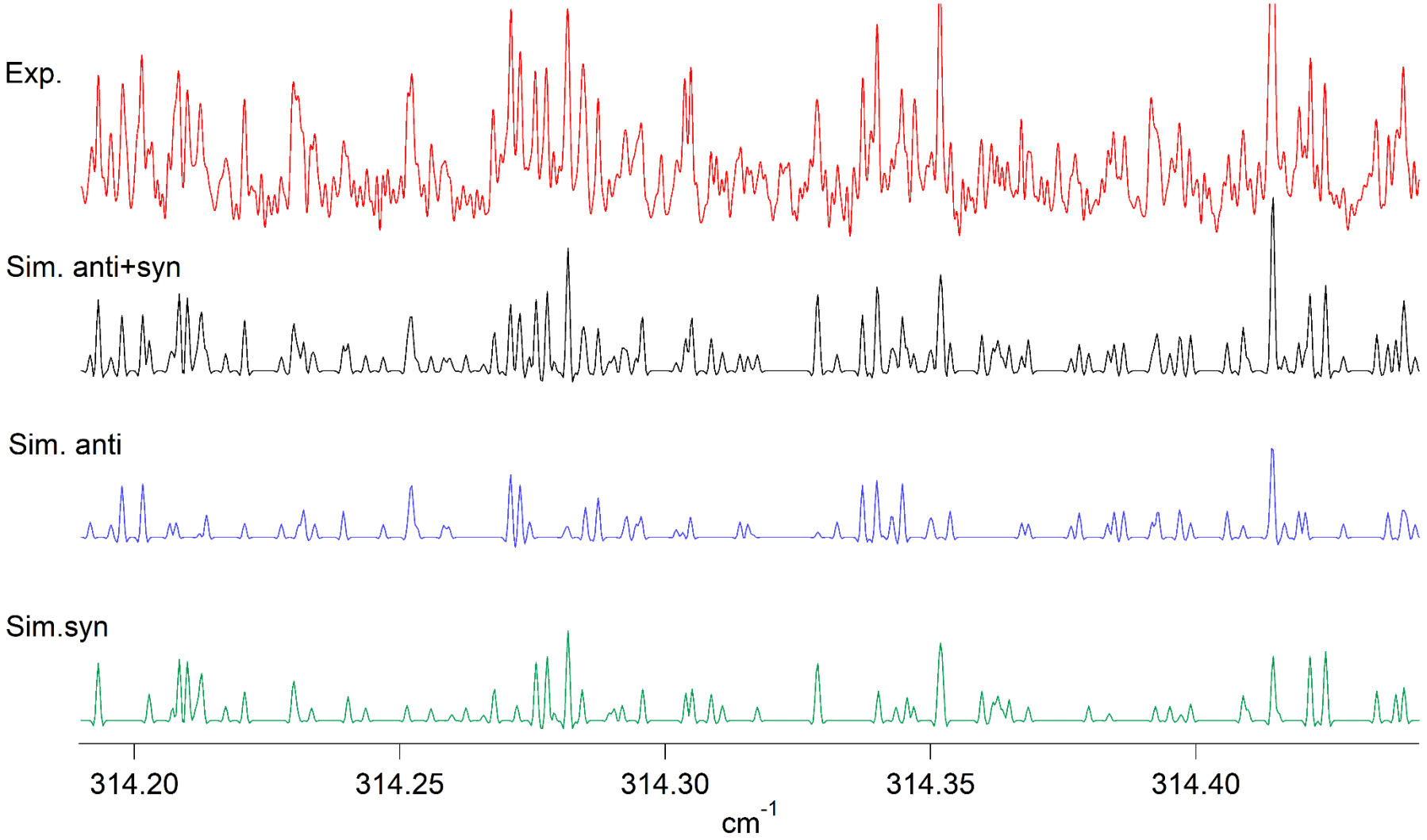
Overview spectra: 240-340 cm^{-1} (7.195-10.193 THz)



Loomis-Wood plots showing patterns of the fundamental



Torsional fundamental



~8000 transitions assigned

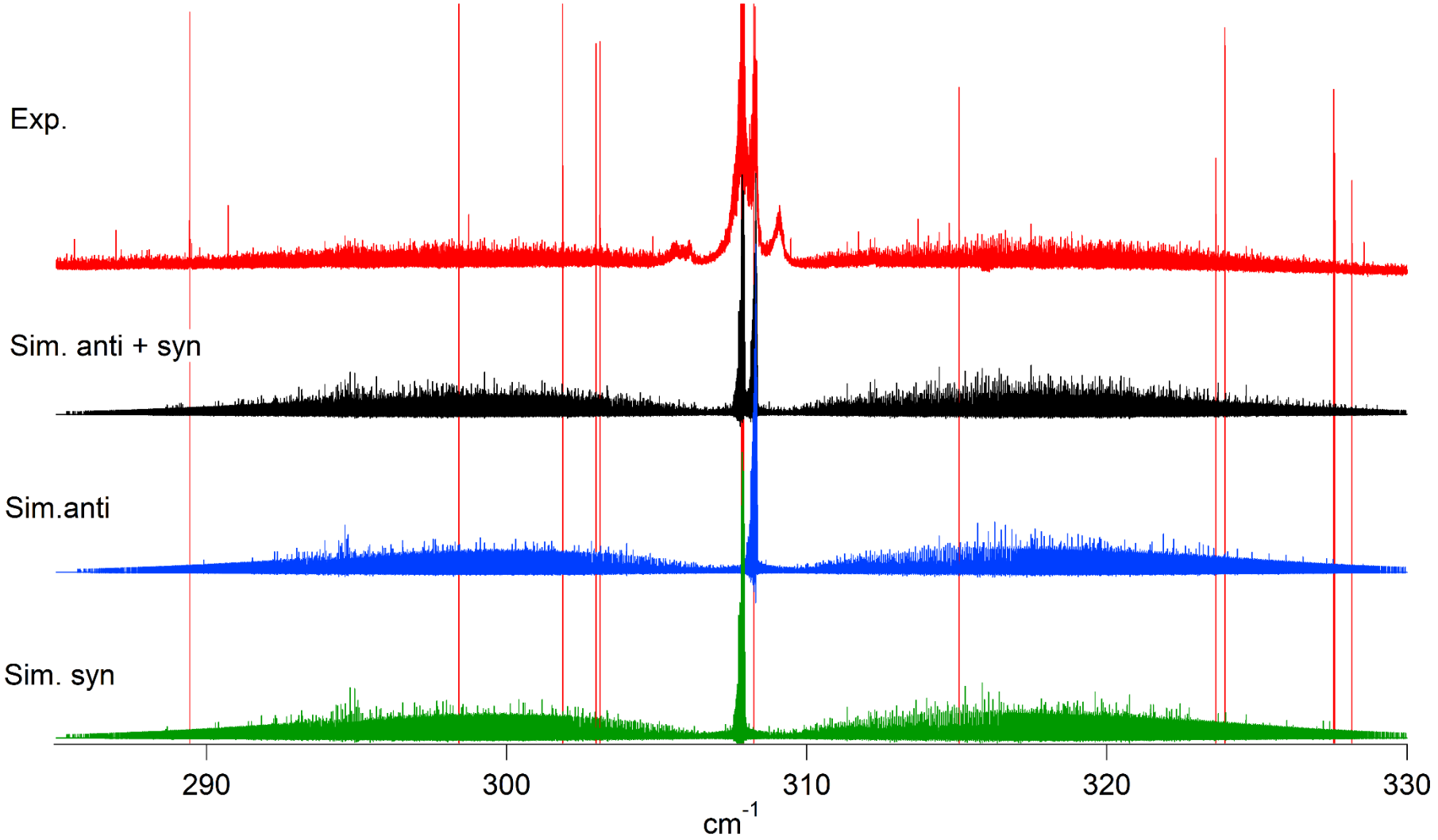
Spectroscopic parameters of the ground state and the first excited torsional state of o-D-Phenol (THz study)

Watson's A-reduction, I^r-representation

	Anti		*Syn*	
	v=0	v_T =1 (308.3589500(53) cm^{-1})	v=0	v_T =1 (307.9413400(67) cm^{-1})
Rotational constants / cm^{-1}				
A	0.17945460(23)	0.179411200(13)	0.17931970(19)	0.179285160(17)
B	0.08707520(26)	0.086919550(21)	0.08709140(24)	0.086935940(26)
C	0.05863470(43)	0.058617930(25)	0.05862700(49)	0.058611300(31)
Centrifugal distortion constants / 10^{-6} cm^{-1}				
Δ_J	0.00430(17)	0.0043400(72)	0.00400(24)	0.004050(10)
Δ_K	0.02430(32)	0.024300(25)	0.02400(53)	0.023800(38)
Δ_{JK}	0.00600(49)	0.005800(31)	0.00700(77)	0.006900(46)
δ_j	-0.001300(96)	-0.0012700(57)	-0.00140(13)	-0.0014100(78)
δ_k	-0.01200(59)	-0.012500(69)	-0.0140(13)	-0.01330(10)
d_{rms} / kHz	0.000137	0.000087	0.000127	0.000087
No. of transitions	1234(Ground state comb. diff.)	7379 (*Anti*+*Syn*)	1275(Ground state comb. diff.)	7379 (*Anti*+*Syn*)

[1]Values without parenthesis held fixed to the respective values of the v = 0.

Torsional fundamental



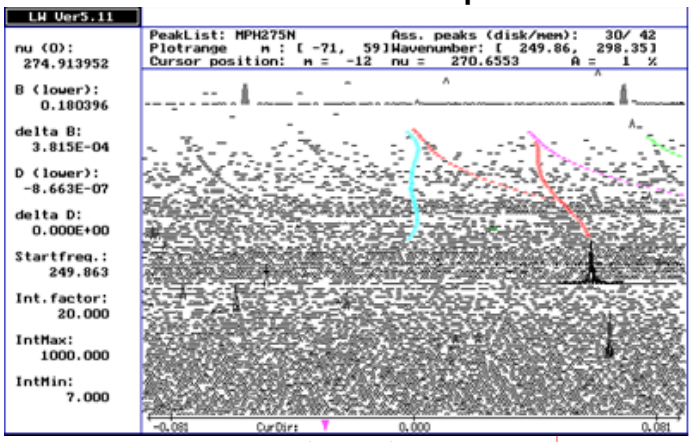
No signs of perturbations

Overview spectra: 240-340 cm^{-1} (7.195-10.193 THz)

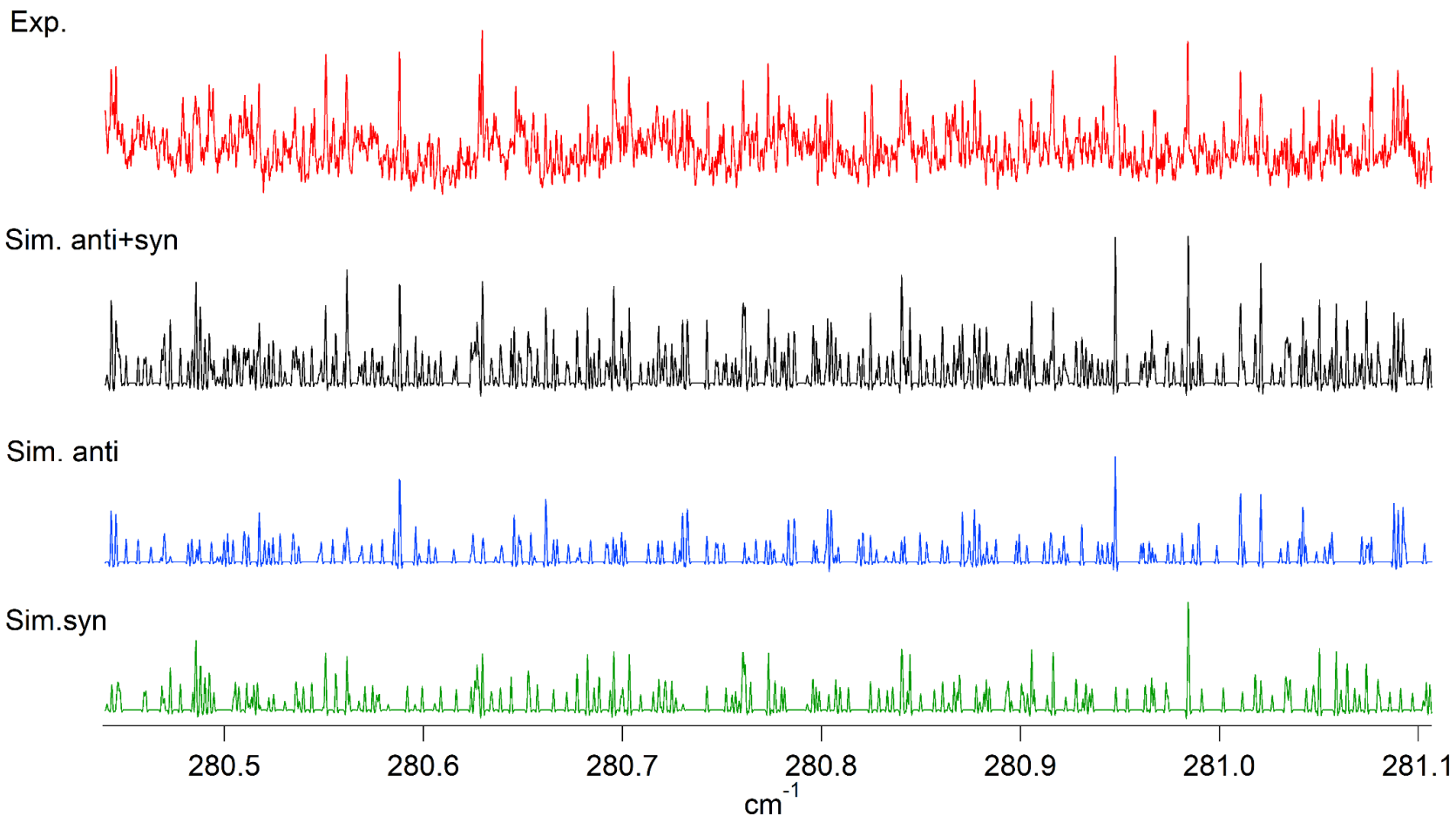
Frequency /THz

6.8952 7.7946 8.3942 8.9938 9.5934 10.1929

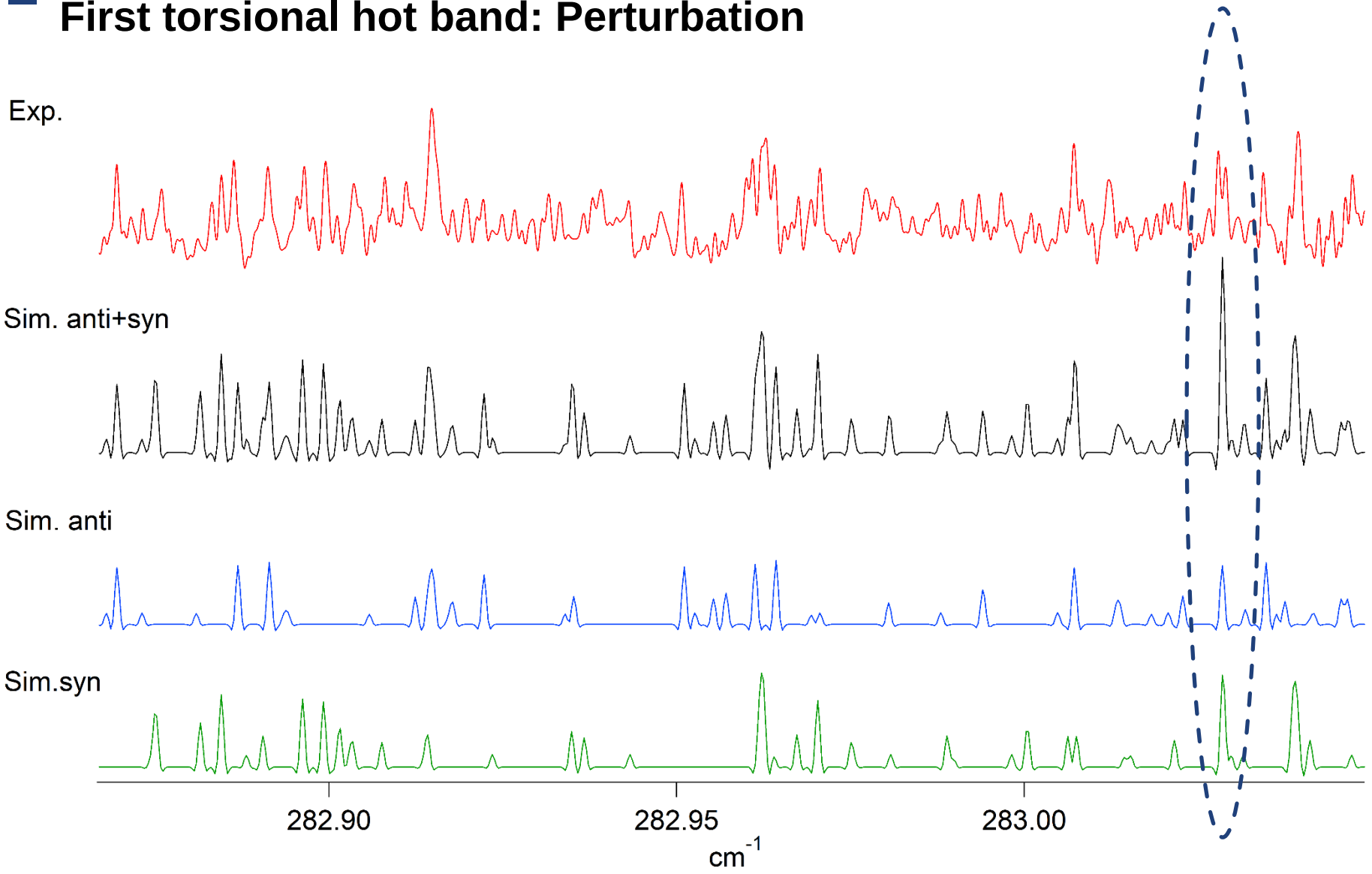
Loomis-Wood plots showing patterns of the hot band



First torsional hot band



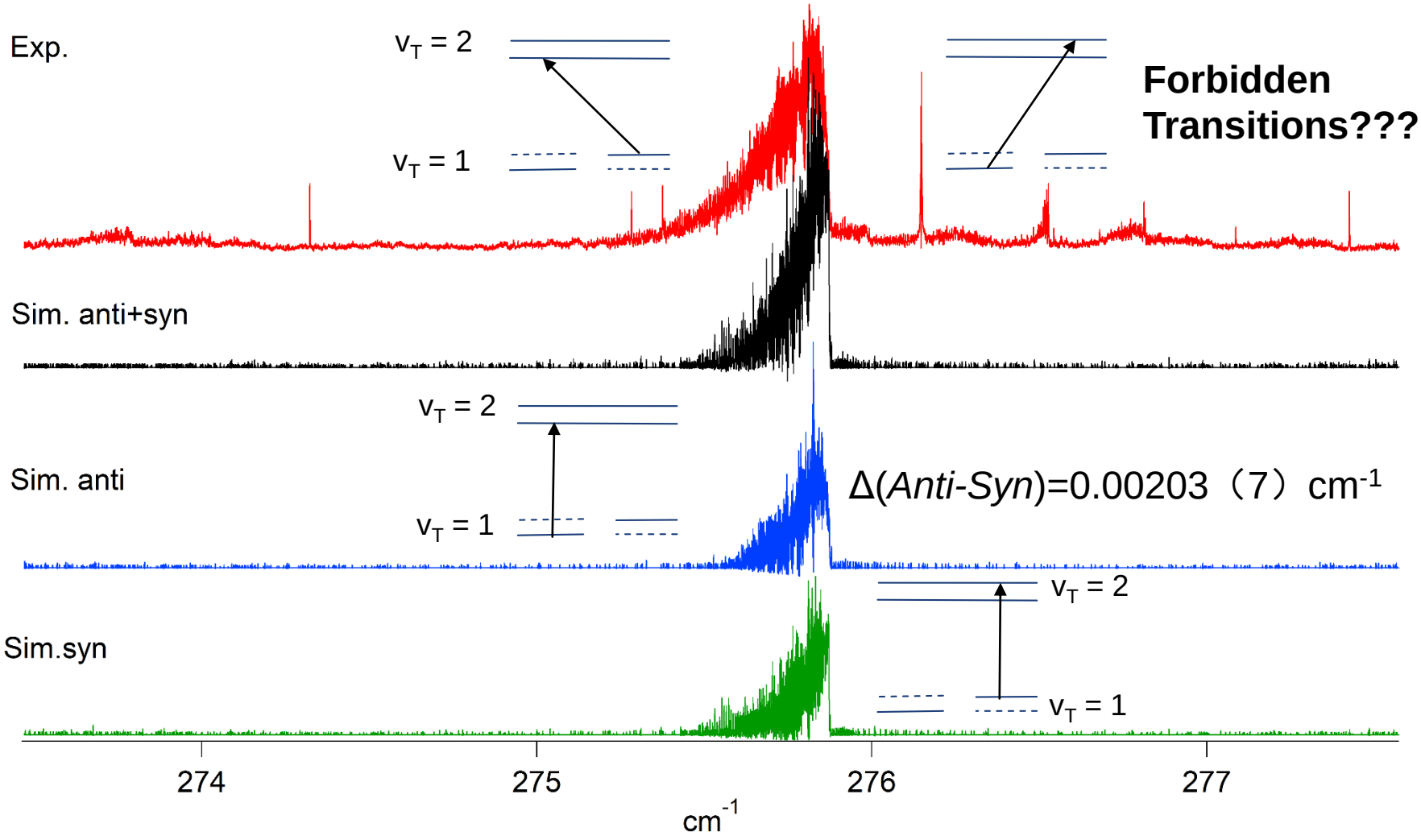
First torsional hot band: Perturbation



Spectroscopic parameters of the second excited torsional state of m-D-Phenol

	Anti		*Syn*	
	v_T =1	v_T =2	v_T =1	v_T =2
Band origin		275.876420(37)		275.874390(28)
Rotational constants / cm^{-1}				
A	0.17941150(14)	0.17946720(14)	0.17928470(16)	0.179145000(95)
B	0.08691930(16)	0.08677500(22)	0.08693600(19)	0.08678980(45)
C	0.05861700(38)	0.05860580(30)	0.05861100(43)	0.05861290(72)
Centrifugal distortion constants / 10^{-6} cm^{-1}				
Δ_J	0.00420(12)	0.00420[1]	0.00430(15)	0.00670(17)
Δ_K	0.02430(25)	0.04350(18)	0.02430(31)	0.00590(28)
Δ_{JK}	0.00600(38)	0.00250(19)	0.00600(46)	0.00400(43)
δ_j	-0.001300(60)	-0.001300	-0.001400(73)	-0.001400
δ_k	-0.01200(42)	-0.01200	-0.01300(53)	-0.01300
d_{rms} / cm^{-1}	0.000119	0.000297	0.000113	0.000297
No. of transitions	1686 (Upper state comb. diff. from the fundamental)	2132 *(Anti+Syn)*	1245 (Upper state comb. diff. from the fundamental)	2132 *(Anti+Syn)*

[1]Values without parenthesis held fixed to the respective values of the v_T =1.

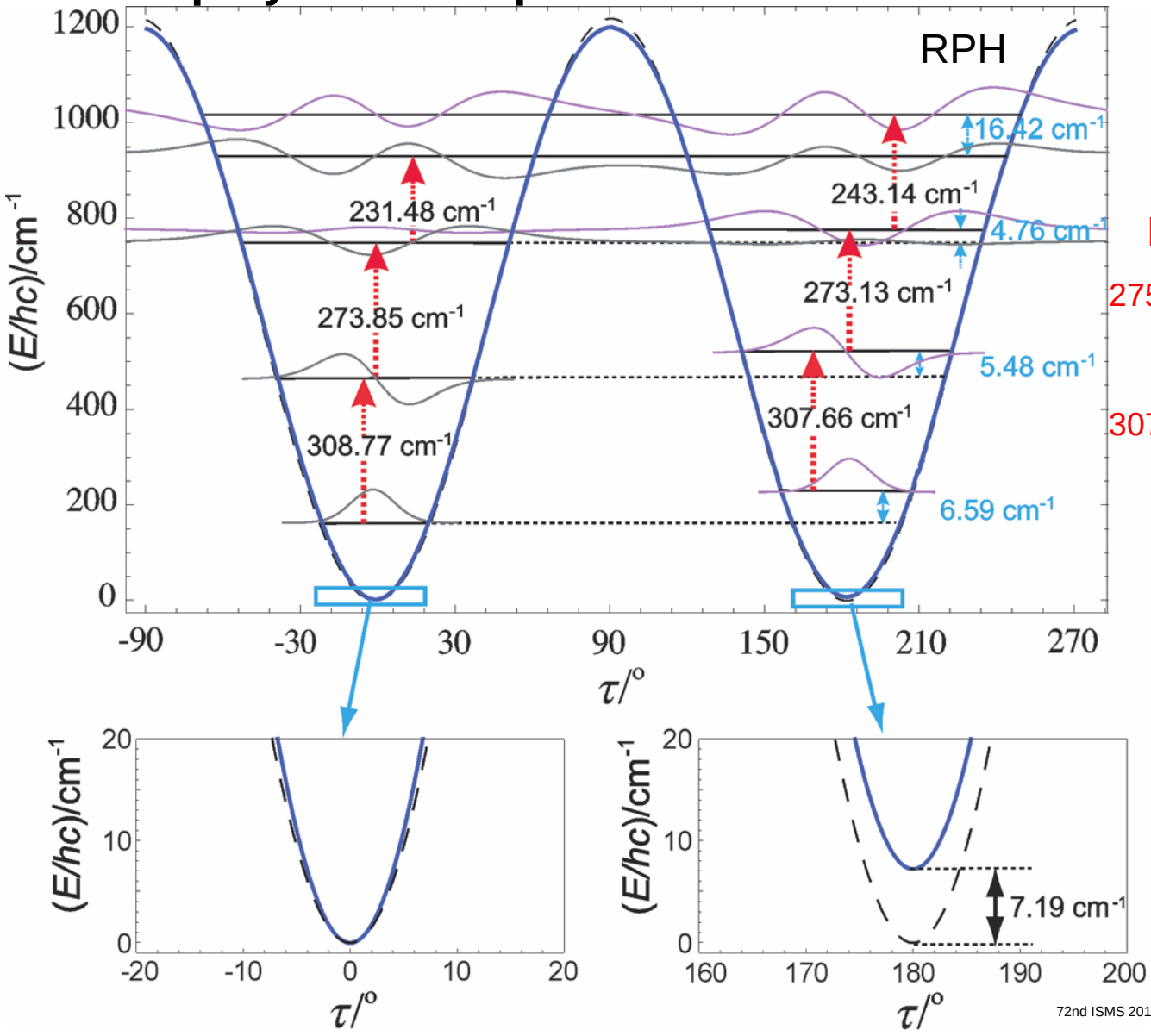

Exp.
$v_T = 2$
$v_T = 1$
Forbidden Transitions???
Sim. anti+syn
$v_T = 2$
Sim. anti
$v_T = 1$
Δ(*Anti-Syn*)=0.00203（7）cm^{-1}
$v_T = 2$
Sim.syn
$v_T = 1$
274
275
276
277
cm^{-1}

The torsional polyad in o-D-phenol

Exp.

275.876 cm^{-1}

308.359 cm^{-1}

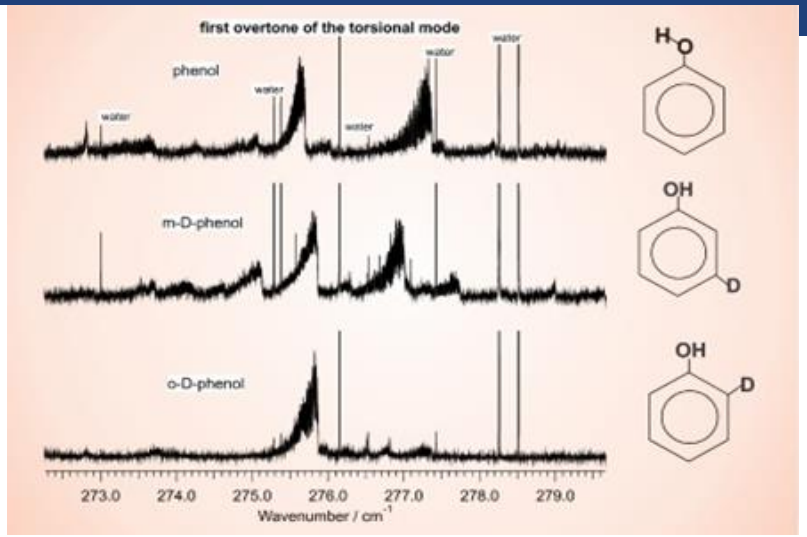


Exp.

275.874 cm^{-1}

307.941 cm^{-1}

Summary



- We have investigated the –OH torsion of phenols using high resolution spectroscopy

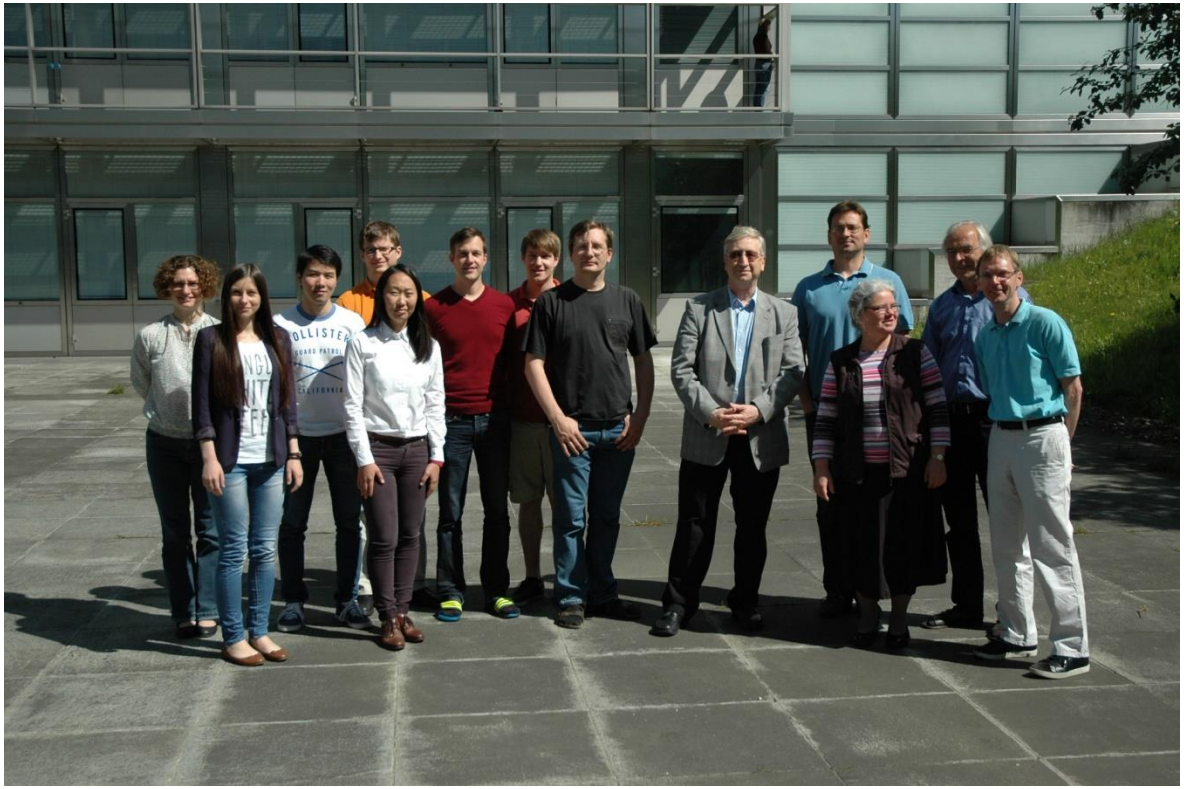
- The assignment of pure rotational and rovibrational spectra led to the accurate determination of vibrational levels of the torsion polyads and assignment of the two isomers

- Particularly, tunneling-switching has been proven and analyzed in m-D-phenol by the observation of “forbidden” transitions and resonances involving upper states but for o-D-phenol only preliminary evidence could be obtained so far for this effect .

- The effective spectroscopic Hamiltonian parameters provided here can be used to improve effective potentials for this prototypical system

Acknowledgement

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



MOLIM MOLECULES IN MOTION

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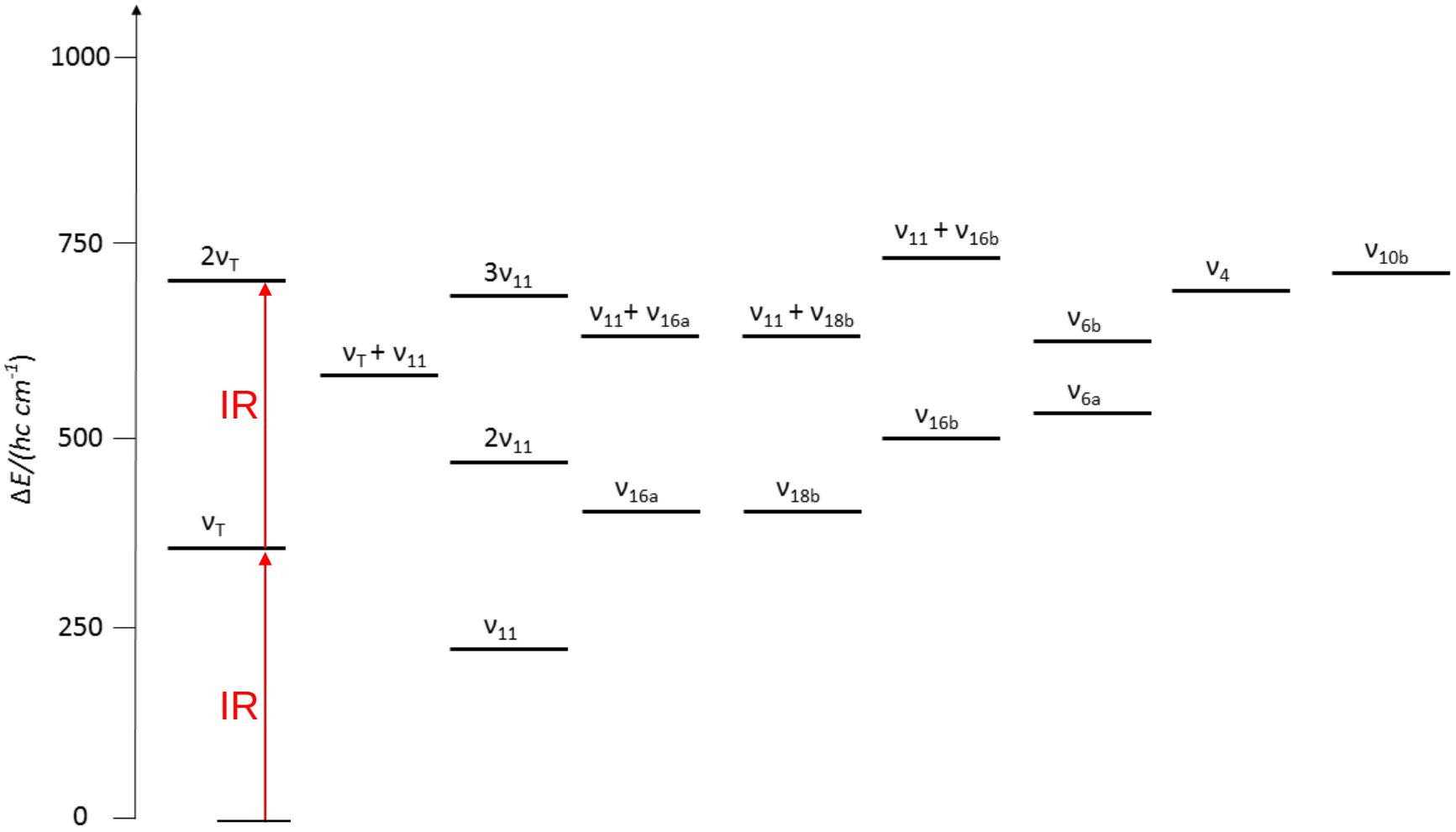
FNSNF FONDS NATIONAL SUISSE SCHWEIZERISCHER NATIONALFONDS FONDO NAZIONALE SVIZZERO SWISS NATIONAL SCIENCE FOUNDATION

erc European Research Council

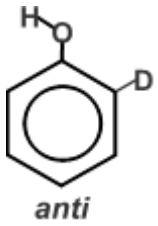
ETH Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich

All low energy levels in o-D-phenol



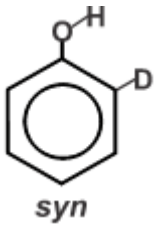
harmonic frequencies calculated at B3LYP/cc-pVTZ level

Assignment of the -*syn* and -*anti* structures



anti

or

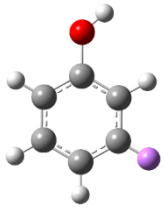


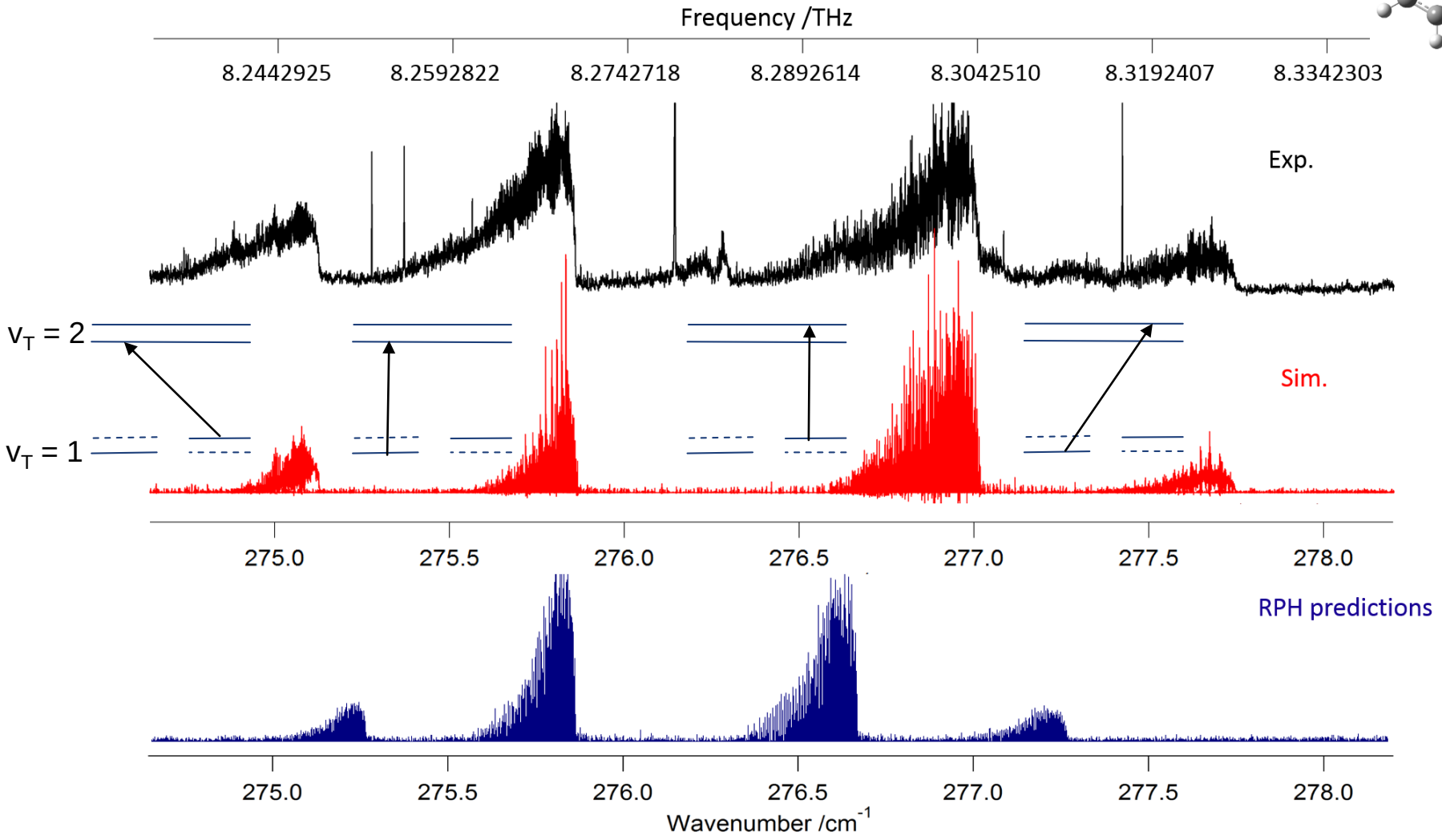
syn

?

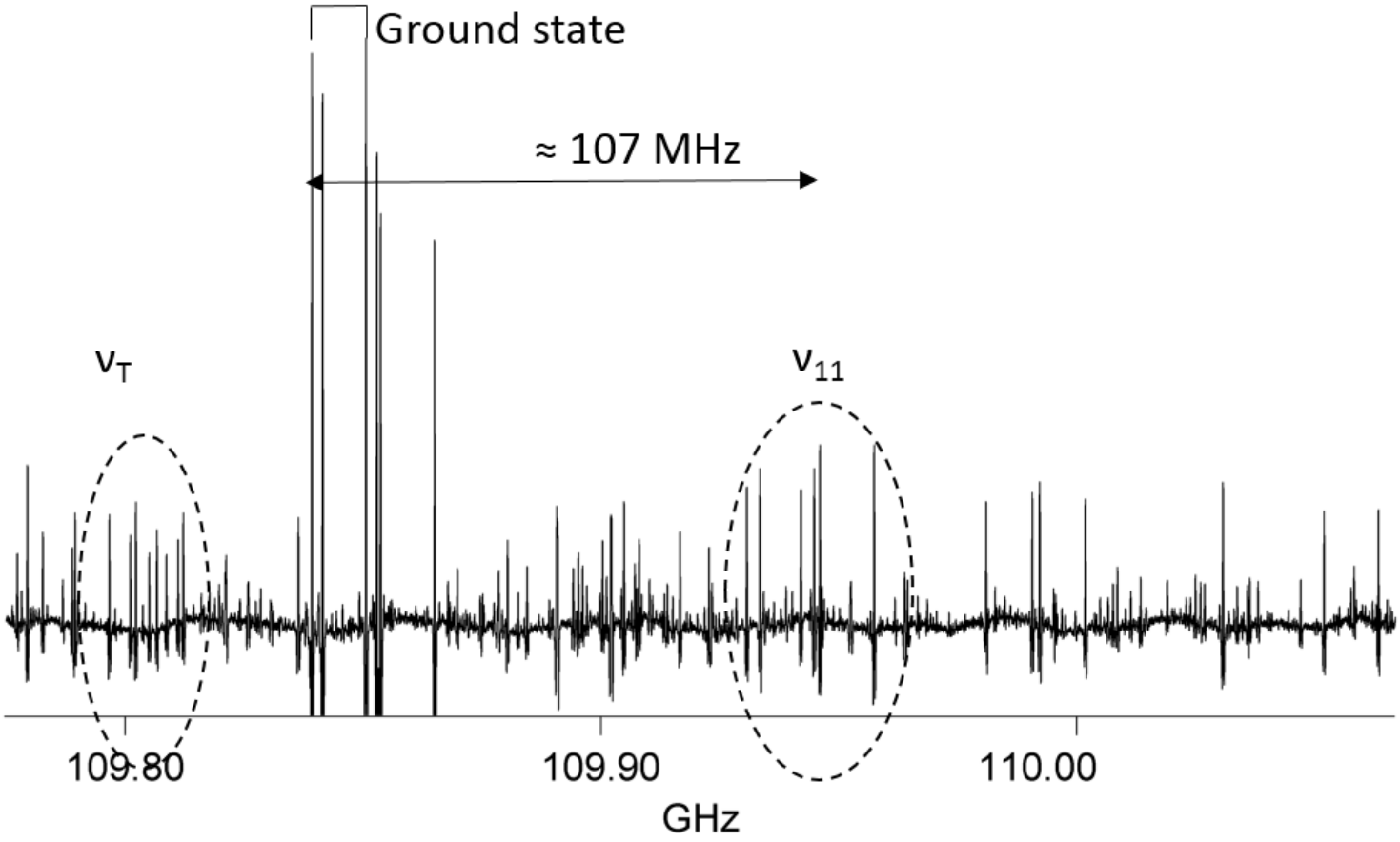
	v=0		v_T =1	
	Exp.	Calc.(RPH)	Exp.	Calc.(RPH)
ΔA / (MHz)	4.08	3.95	3.84	4.38
ΔB	-0.48	-0.58	-0.49	-0.54
ΔC	0.21	0.22	0.19	0.21

“Forbidden” tunneling-rotation-vibration transitions in m-D-phenol

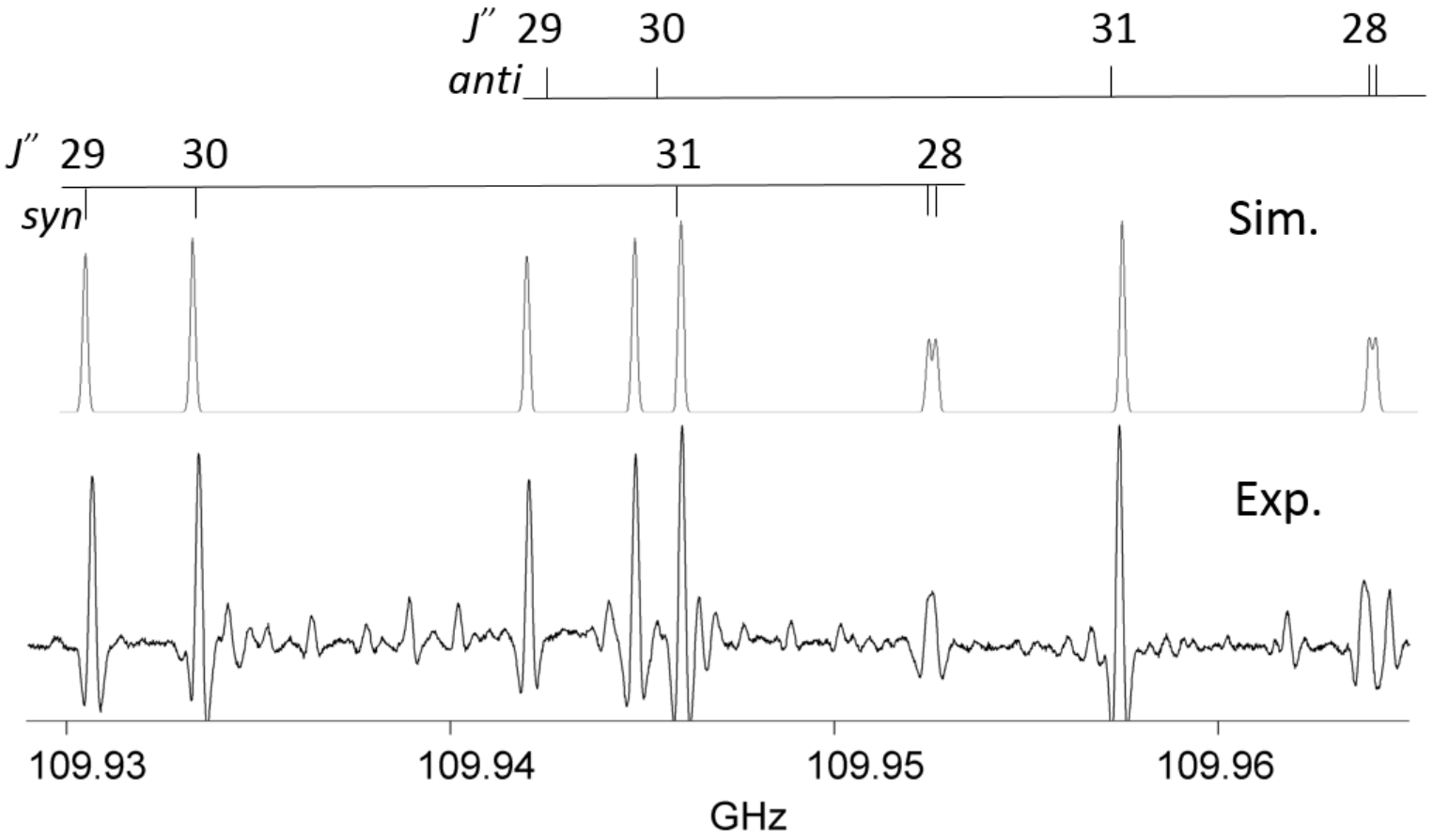




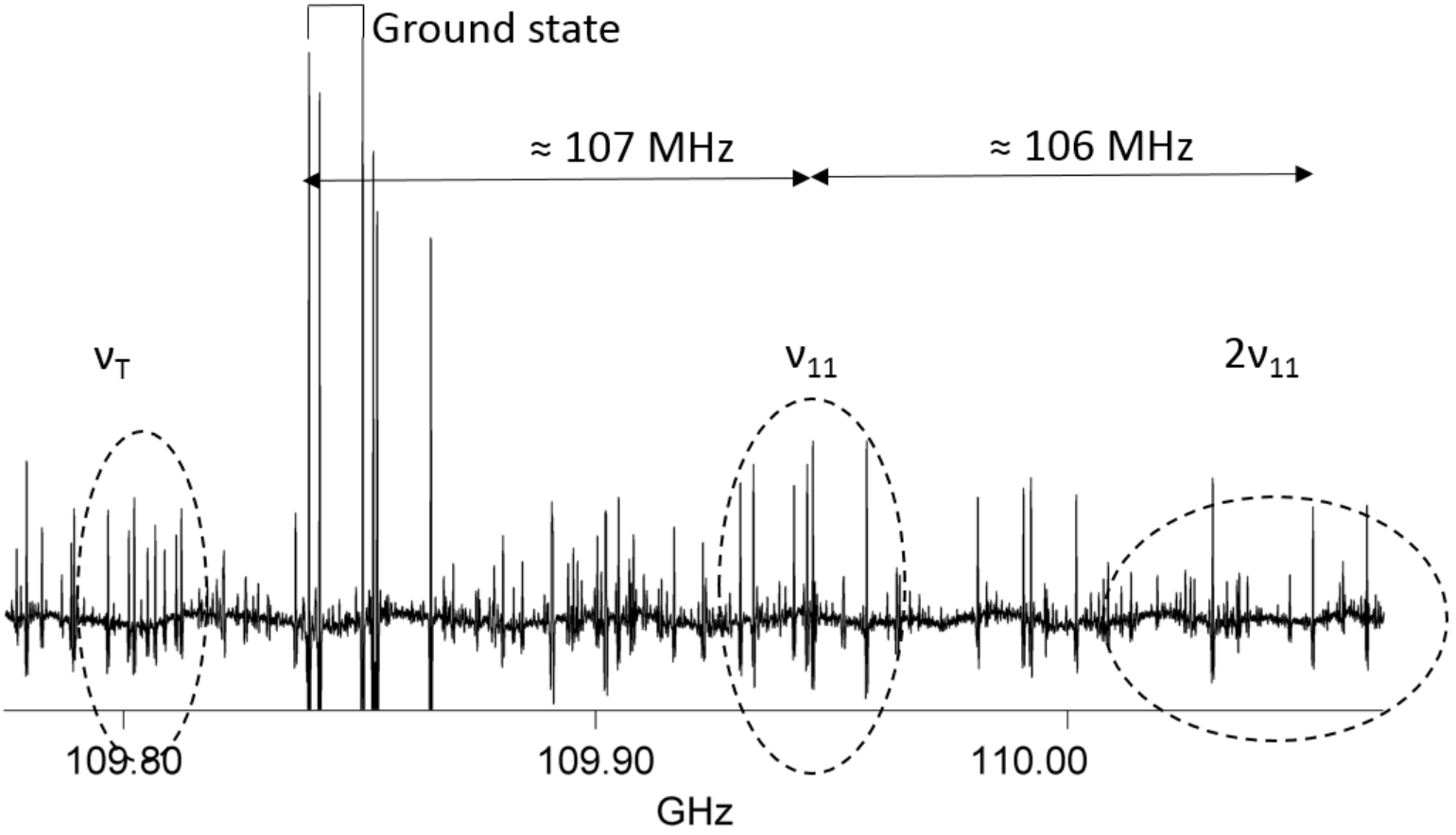
Vibrational satellites: v_{11} mode



Vibrational satellites: v_{11} mode



Vibrational satellites: v_{11} mode



Vibrational satellites: v_{11} mode