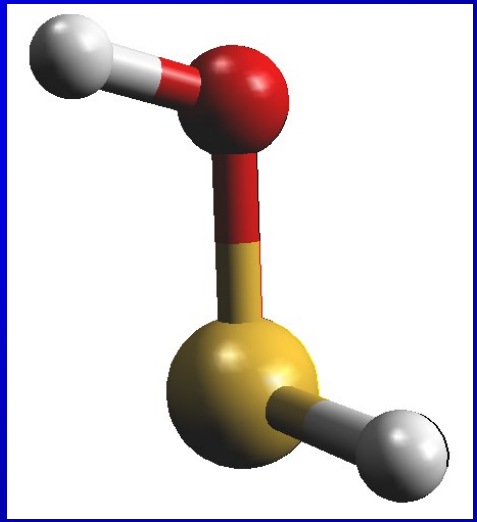
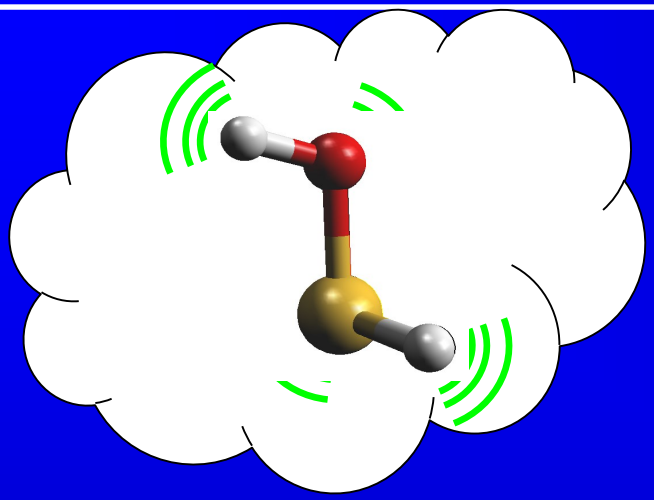
Peculiar Traits of HSOH in its Rotational–Torsional Spectrum above 1 THz

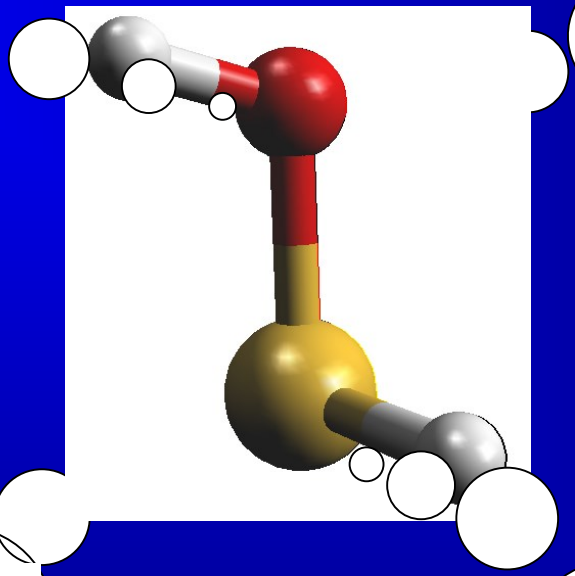


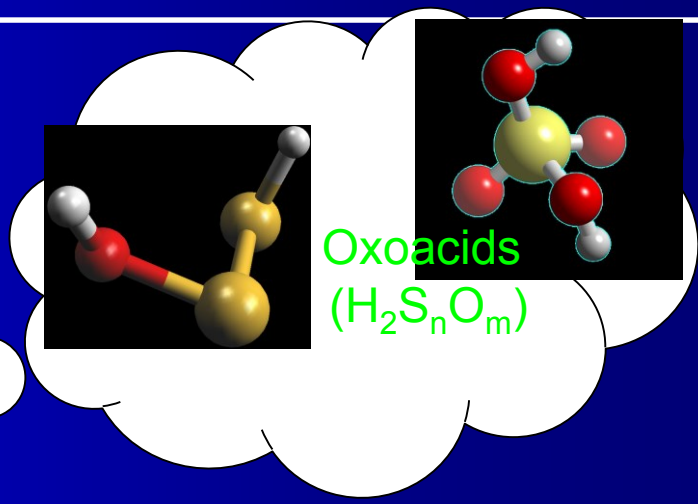
O. Baum[a], M. Koerber[a], S. Schlemmer[a], S.N. Yurchenko[b], W. Thiel[c], P. Jensen[d], K.M.T. Yamada[e], and T. F. Giesen[a]

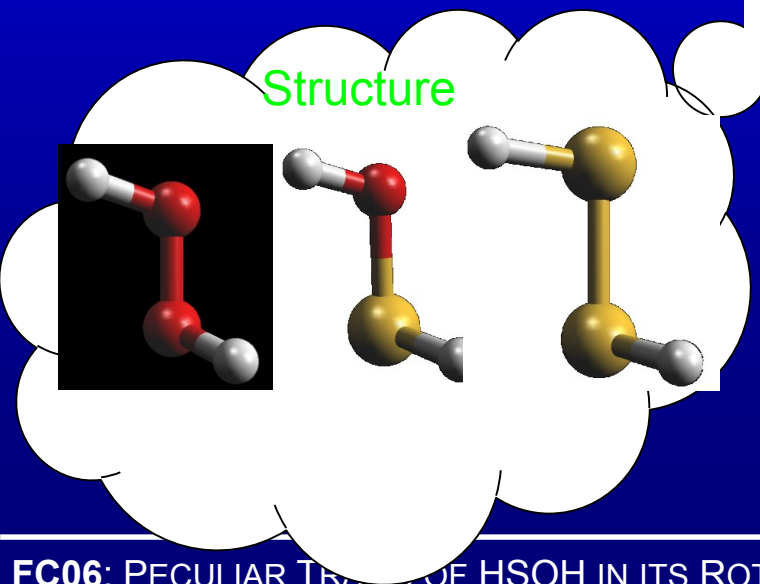
[a] I. Physikalisches Institut, Universität zu Köln, Germany
[b] Institut für Physikalische Chemie und Elektrochemie, TU Dresden, Germany
[c] MPI für Kohlenforschung, Mülheim an der Ruhr, Germany
[d] Theoretische Chemie, Bergische Universität, Wuppertal, Germany
[e] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba-West, Japan

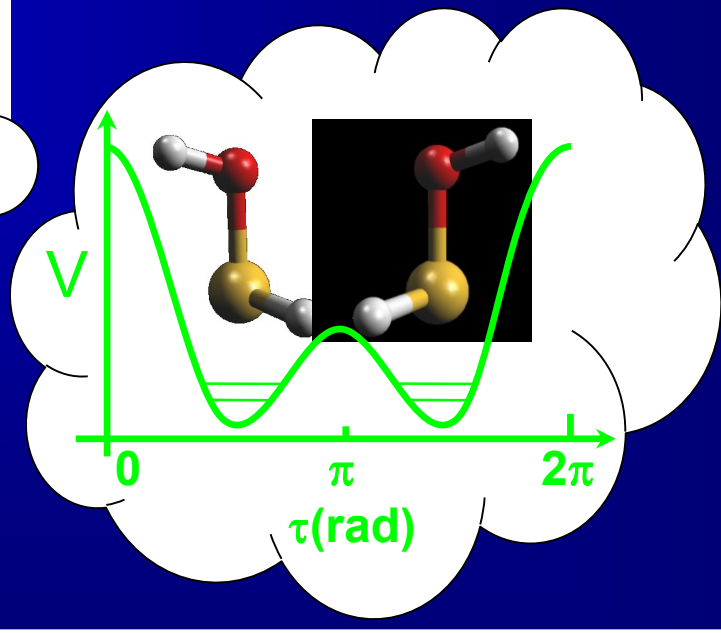
64th International Symposium on Molecular Spectroscopy, Ohio **June, 26. 2009**



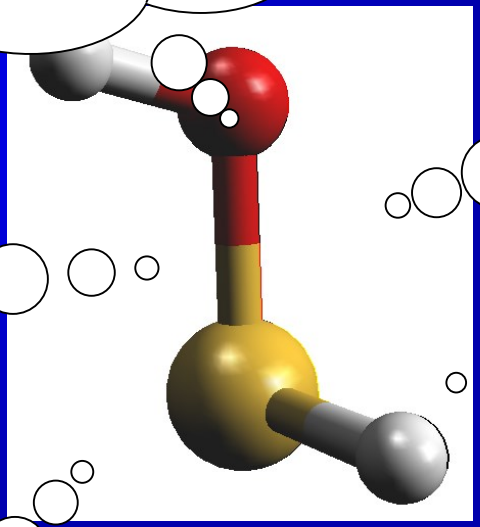


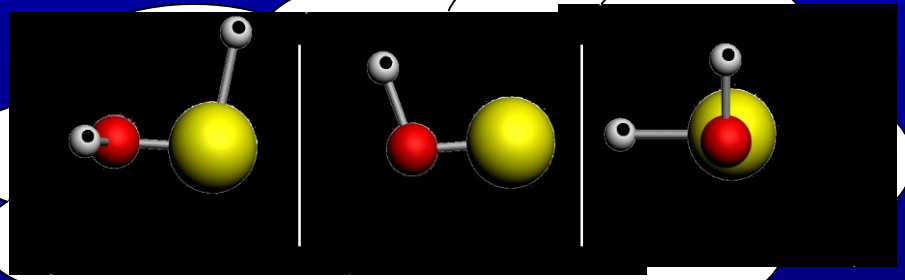

Oxoacids
($H_2S_nO_m$)


Structure


V
0
π
2π
τ(rad)

Properties of HSOH

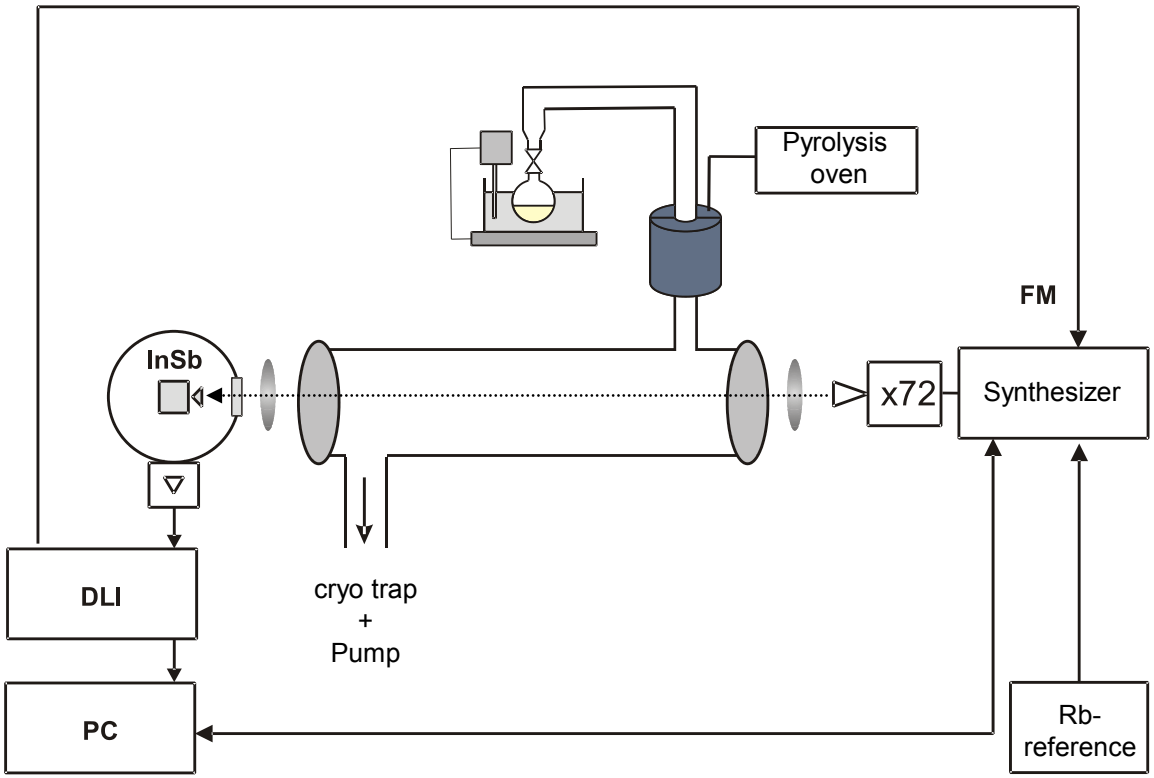




* Baum *et al.*, J. Chem. Phys. (2008)

Winnewisser *et al.*, Chem. Eur. J. (2003) (CCSD(T)/cc-pCVQZ)

Experimental setup



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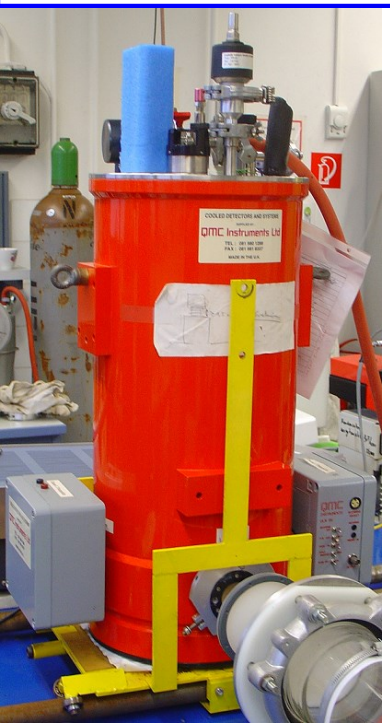
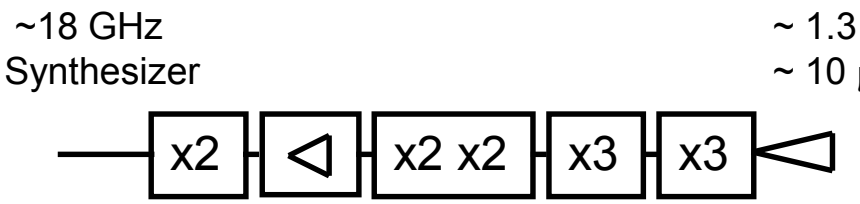
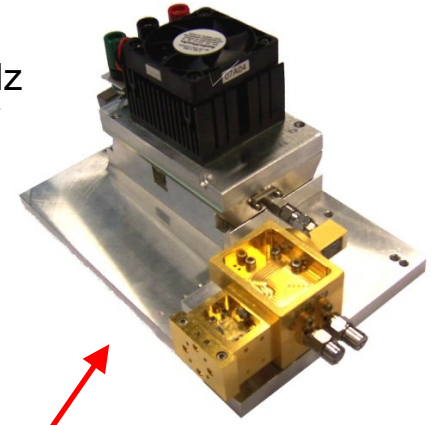
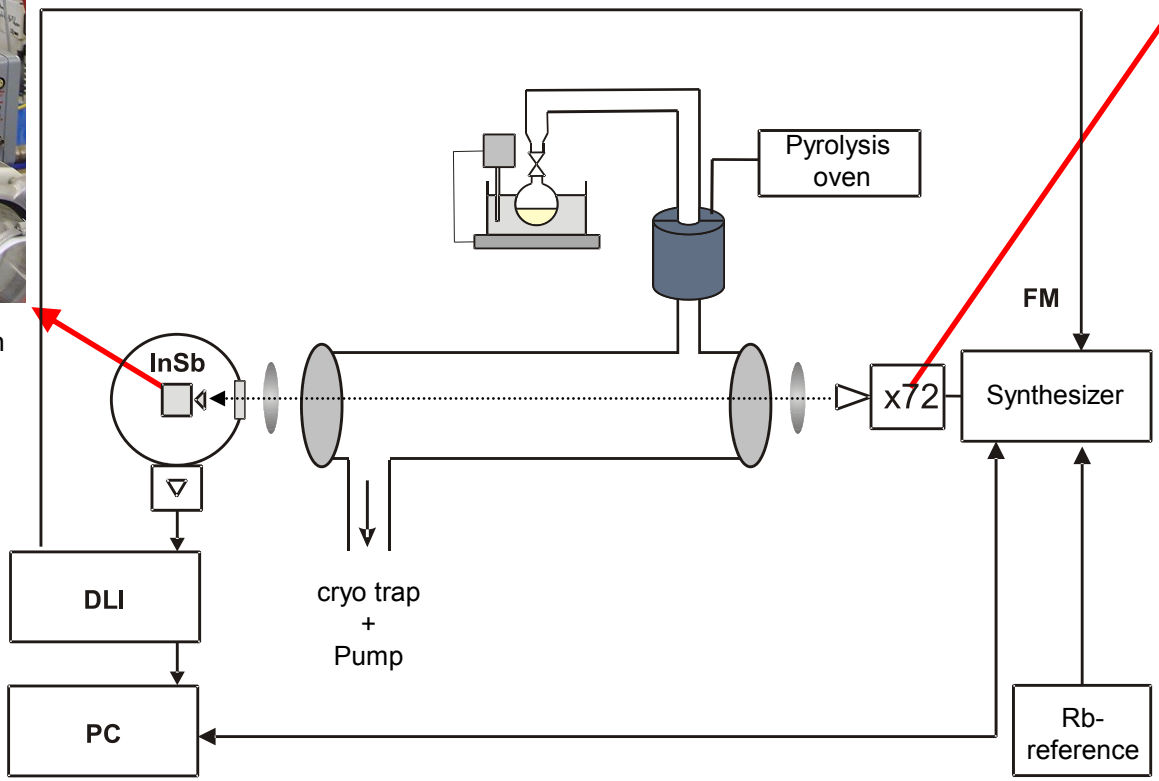


I-He cooled InSb hot electron bolometer (QMC Inc.)





(Virginia Diodes Inc.)



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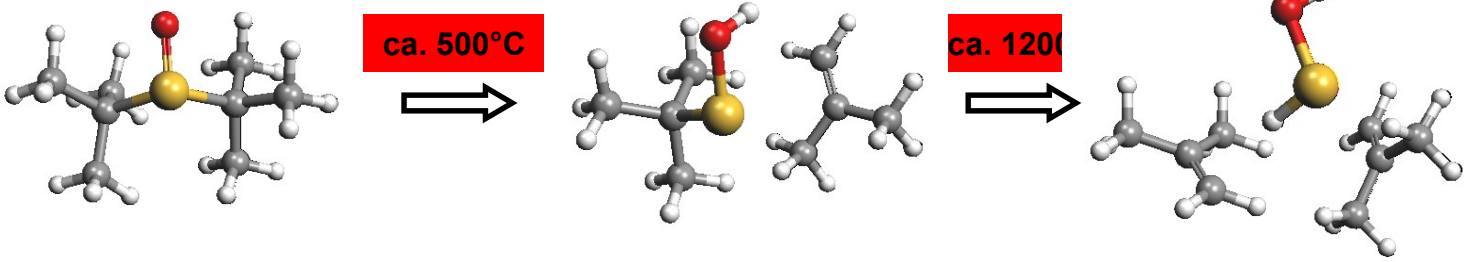
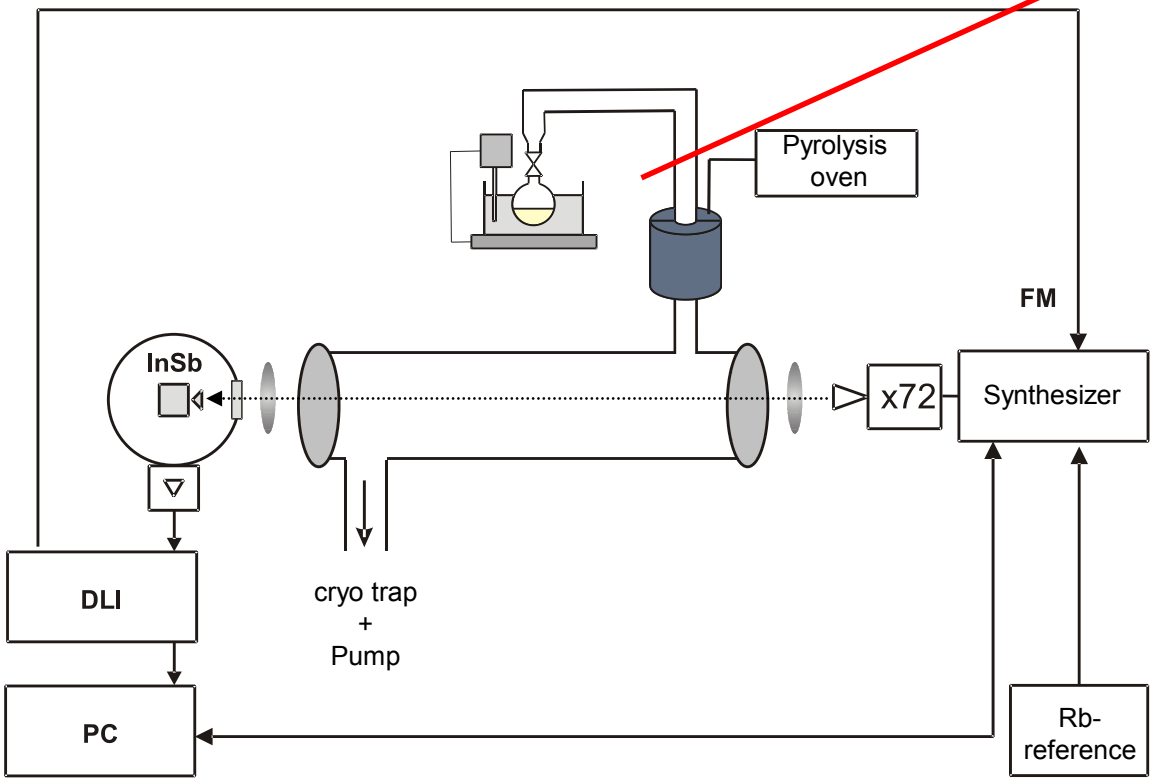


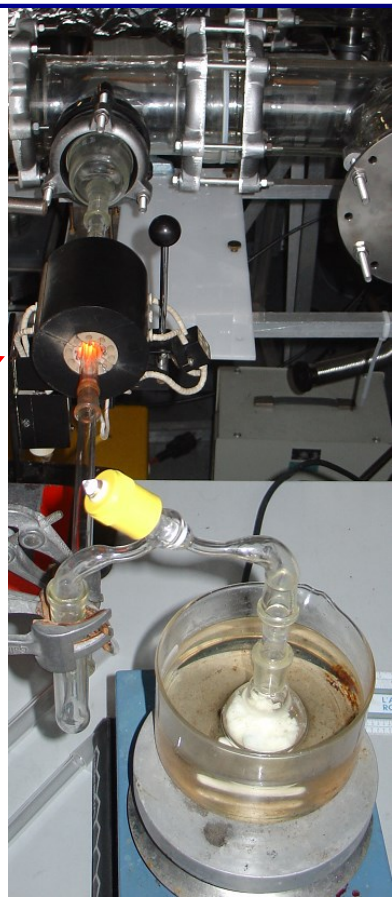
Di-*tert*-butylsulfoxide

tert-Butylsulfenic acid
+ *iso*-Butene

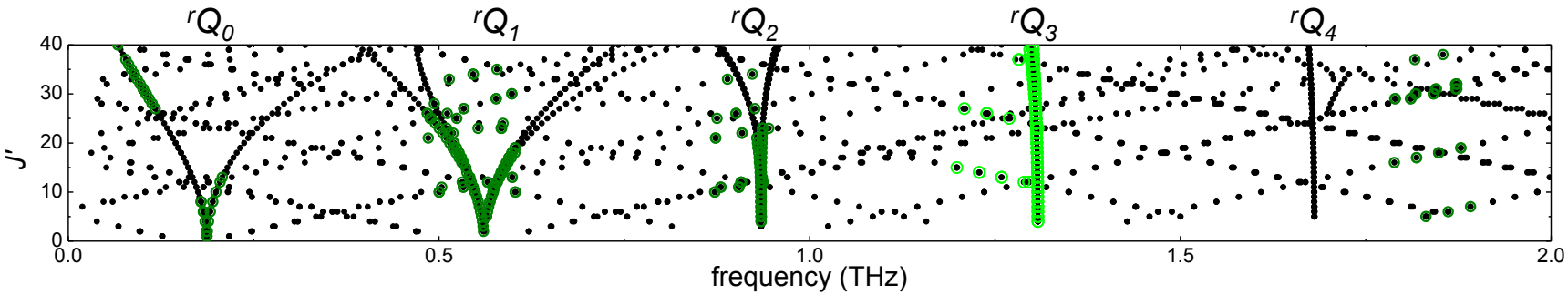
Oxadisulfane
+ 2x *iso*-Butene

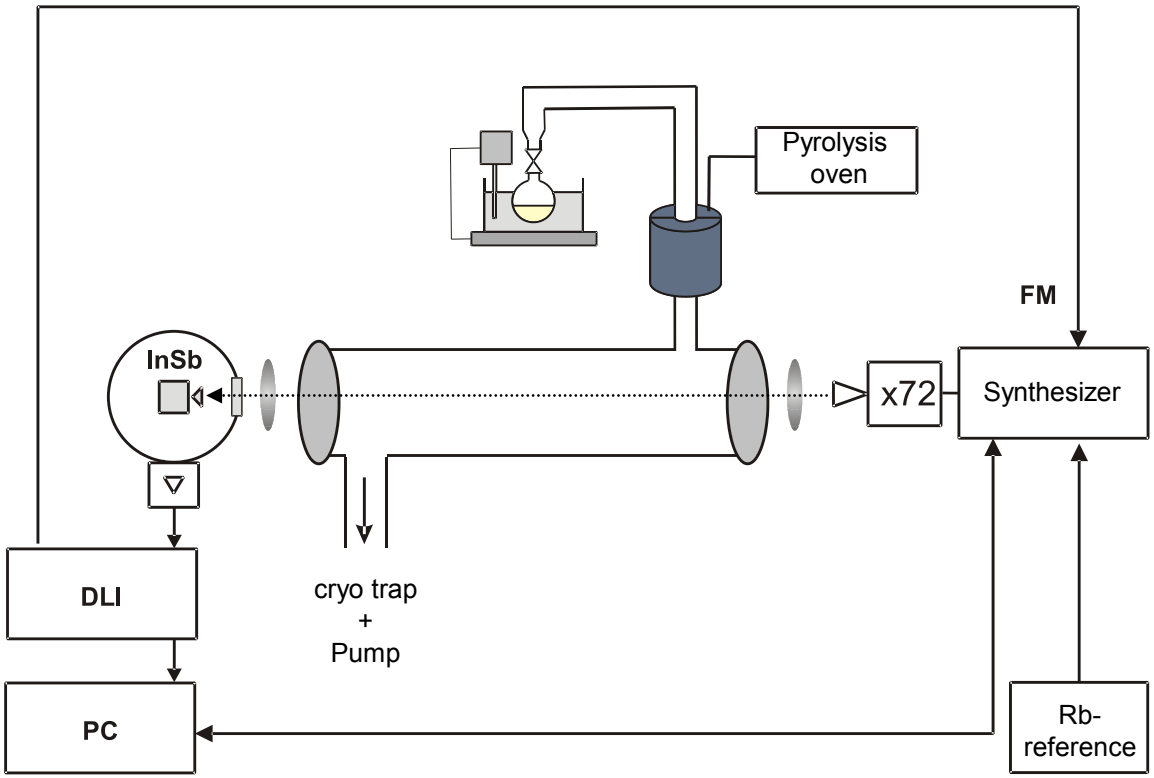
Winnewisser *et al.*, Chem. Eur. J. (2003)
Beckers *et al.*, Chem Eur J. (2005)



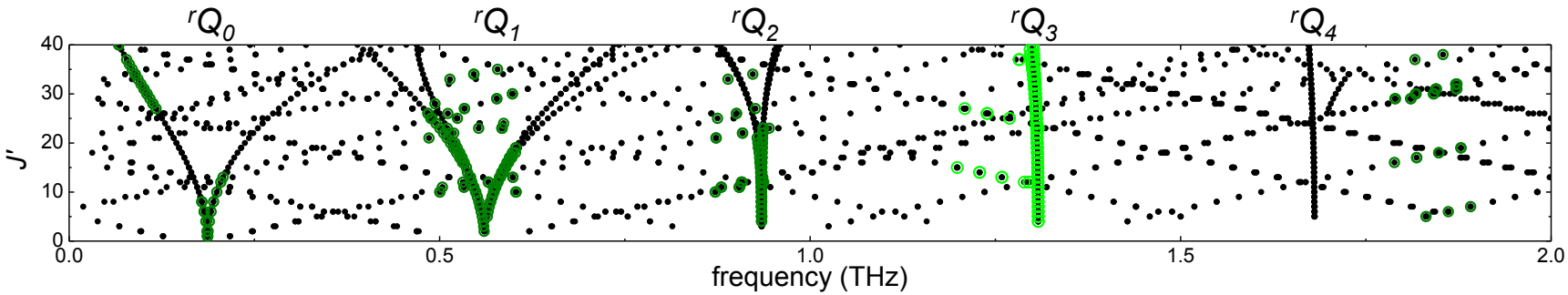


Experimental results



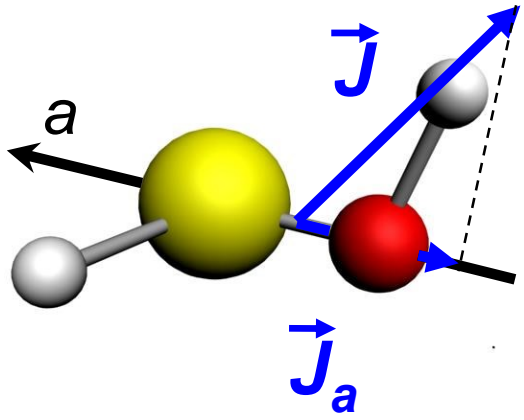


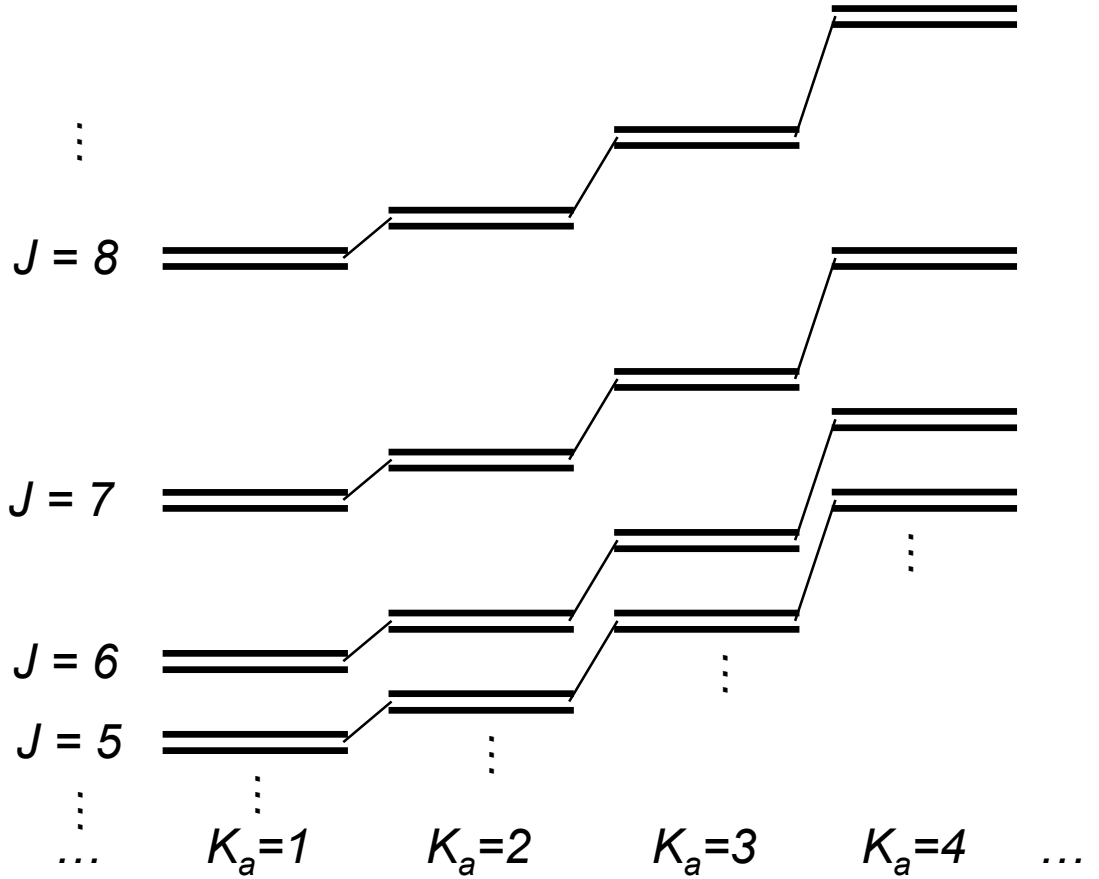
Experimental results



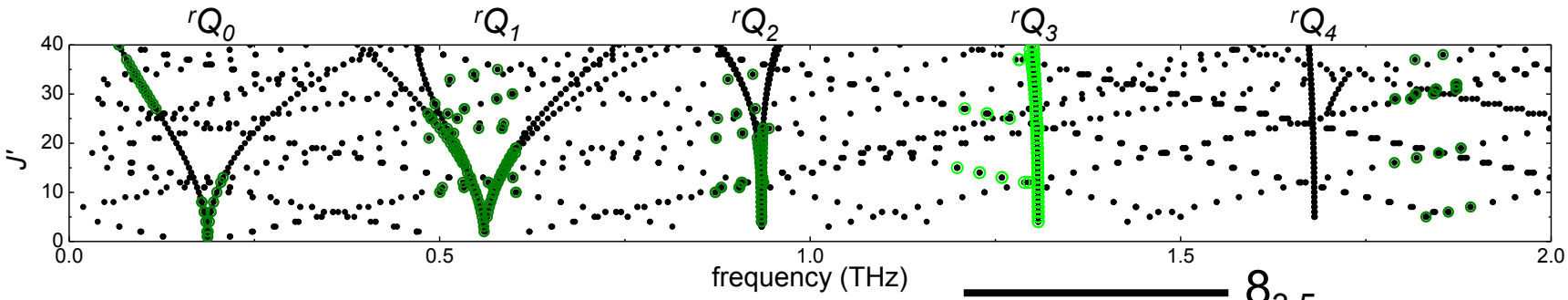
$^rQ_2$-branch

ΔK_a=+1 ΔJ=0 K_a“=2





Experimental results



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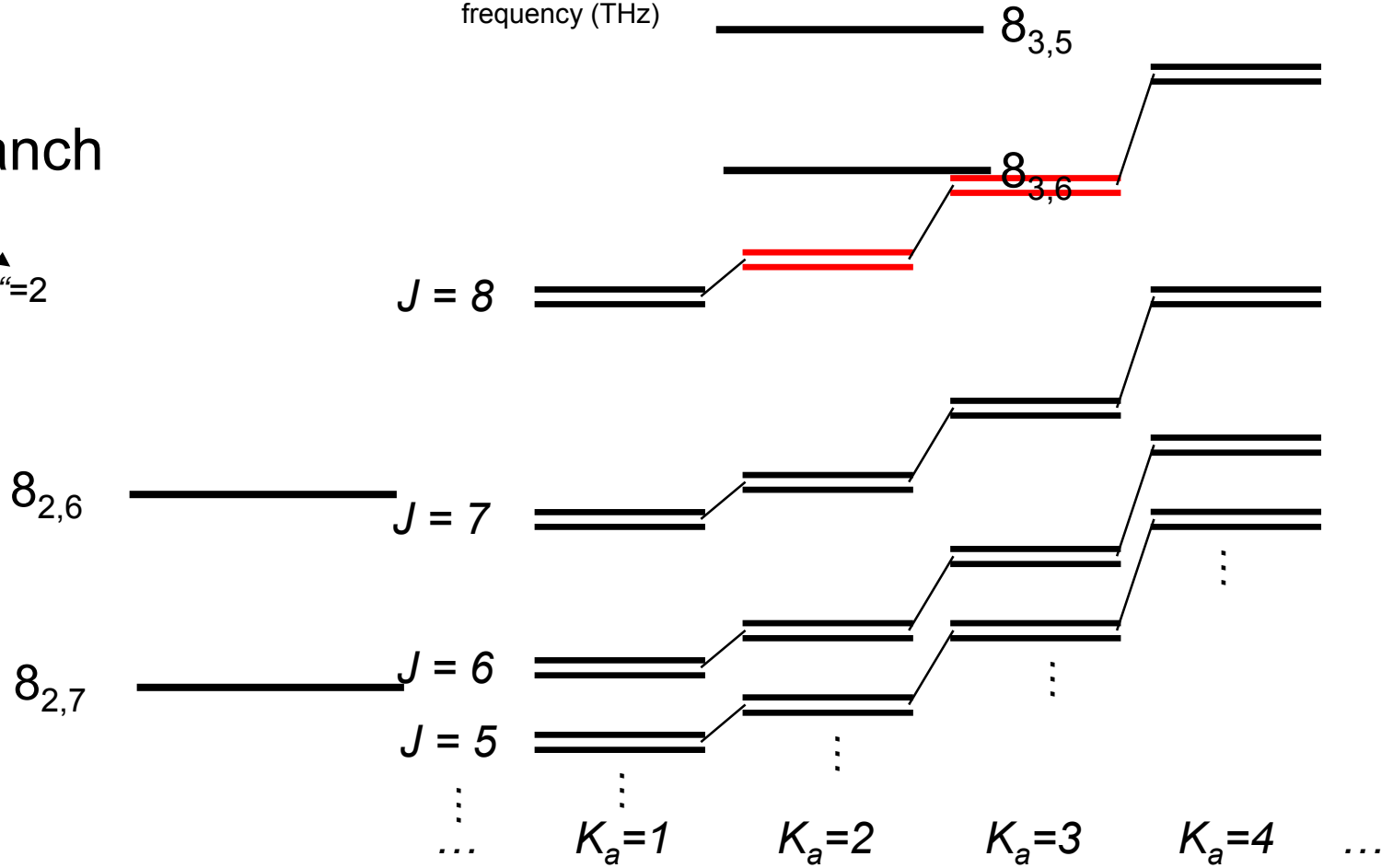
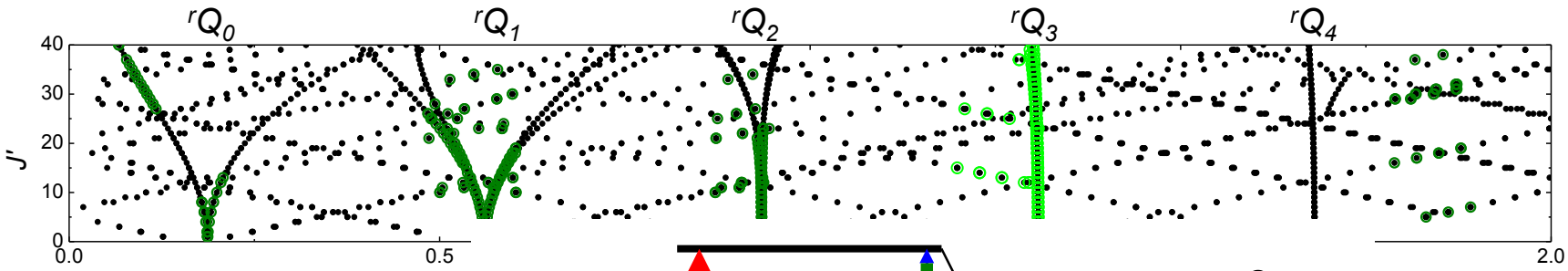


Torsional splitting



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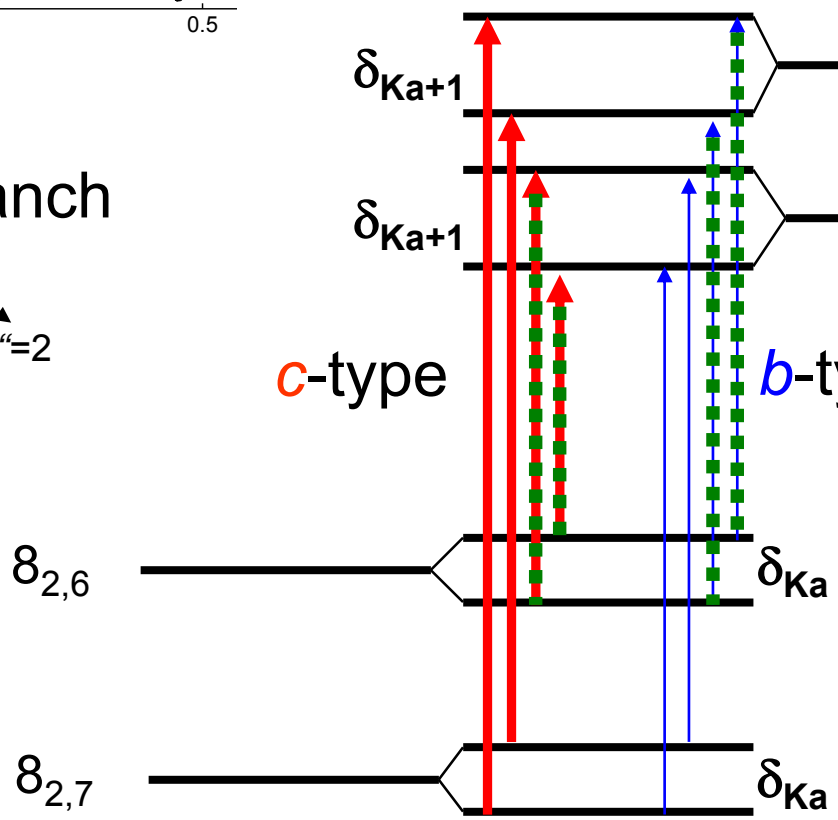
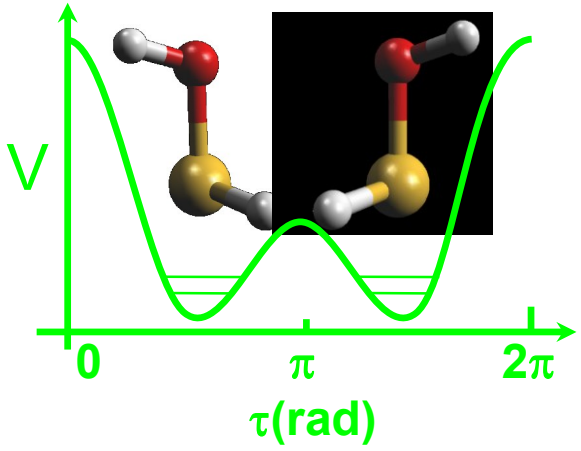


$8_{3,6} \leftarrow 8_{2,6}$

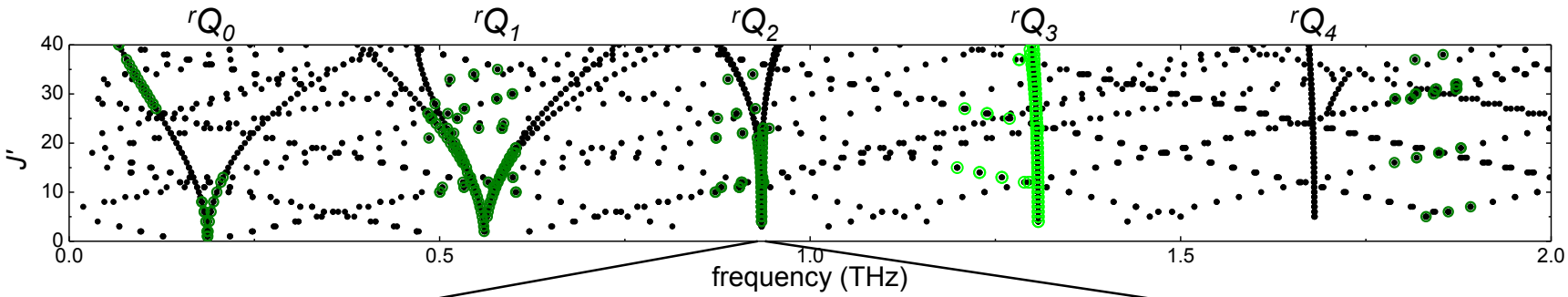
$8_{3,5} \leftarrow 8_{2,6}$

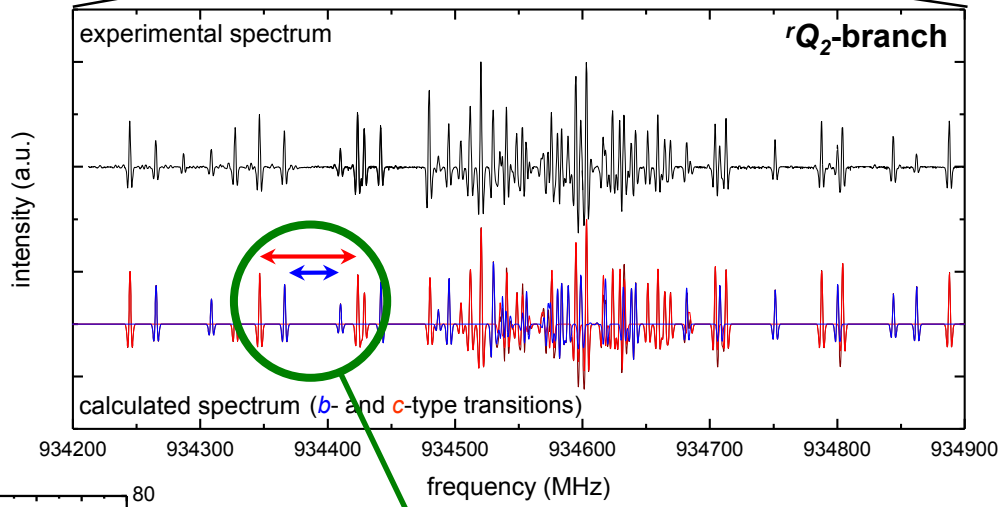


$\Delta\nu(c) = \delta_{Ka+1} + \delta_{Ka}$

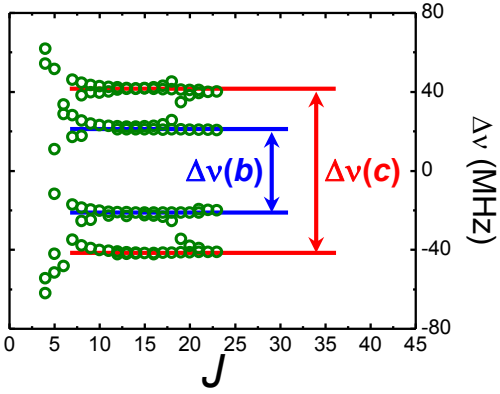
$\Delta\nu(b) = |\delta_{Ka+1} - \delta_{Ka}|$

Torsional splitting





$^{r}Q_2$



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$\Delta\nu(c) = \delta_{Ka+1} + \delta_{Ka}$

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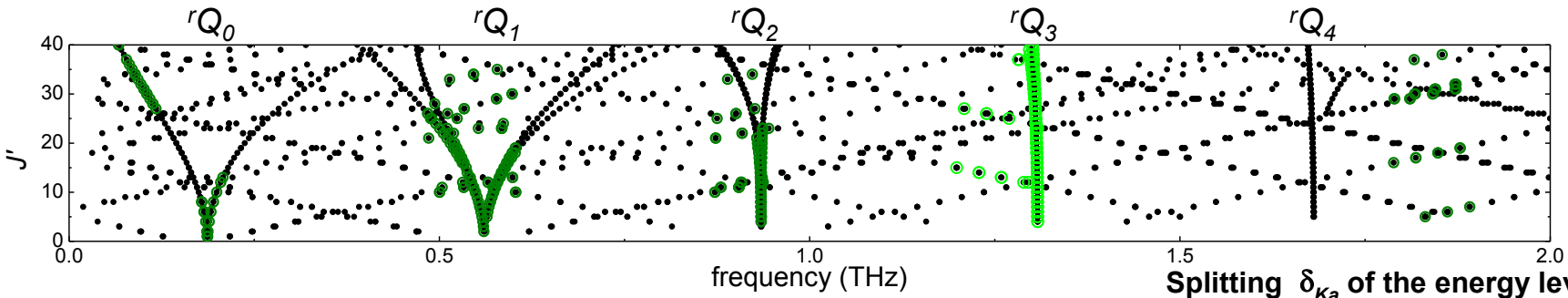
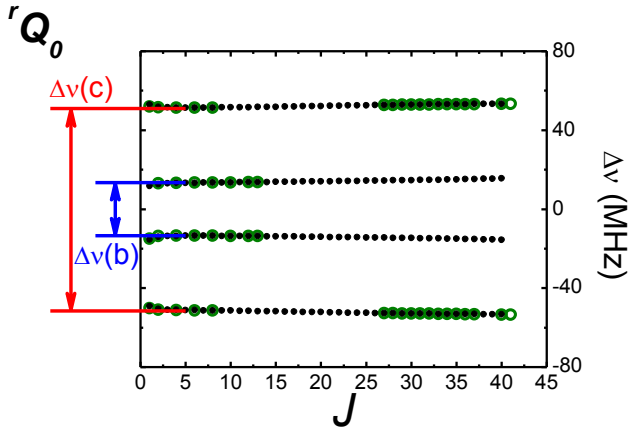
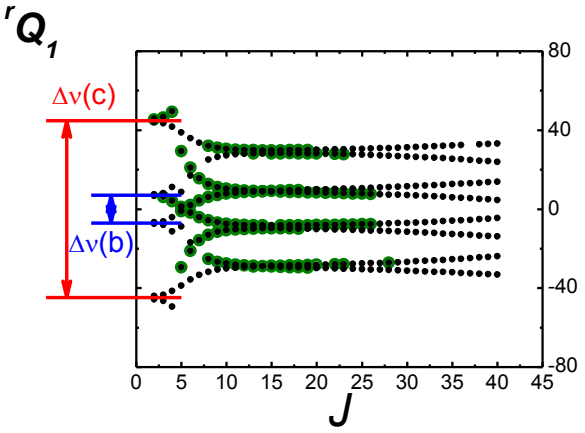
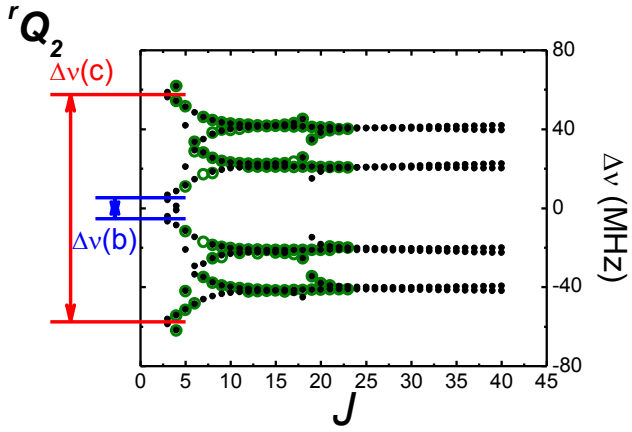
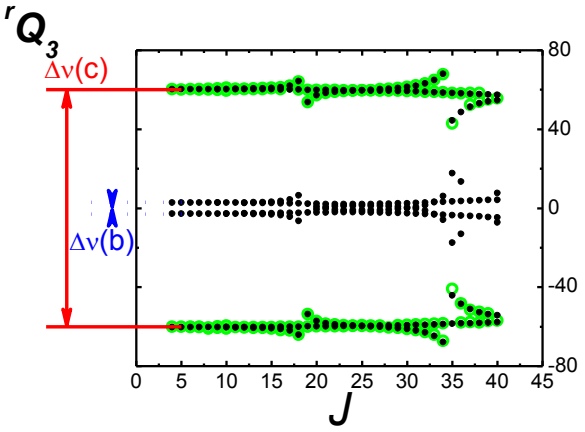
Torsional splitting











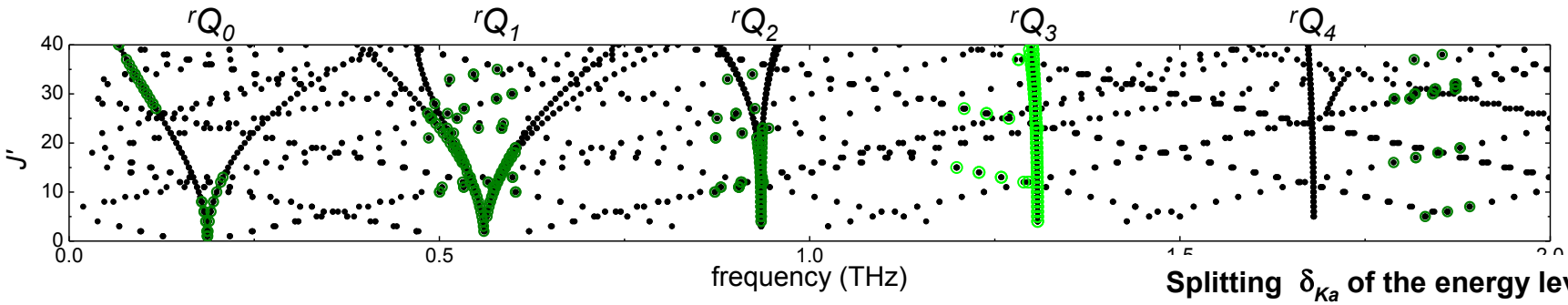
Splitting δ_{Ka} of the energy levels (in MHz) (for $J=K_a$)

K_a	δ_{Ka}^{exp} [this work]	δ_{Ka}^{TROVE} Ovsyannikov *et al.*, J. Chem. Phys. (2008)	δ_{Ka}^{YWJ} Yamada *et al.*, J. Mol. Struct. (2009)
0	64.5	64.5	63.9
1	37.8	37.9	33.3
2	52.1	55.3	50.9
3	62.9	64.0	63.5
4	57.2	58.8	57.3
5	49.0	52.9	49.2
6	60.8	62.1	63.0
7	60.0	61.6	61.5

$$\Delta\nu(c) = \delta_{Ka+1} + \delta_{Ka}$$

$$\Delta\nu(b) = |\delta_{Ka+1} - \delta_{Ka}|$$

Torsional splitting



TROVE

"quantum chemists approach" #

Y W J

"anti quantum chemists approach" #

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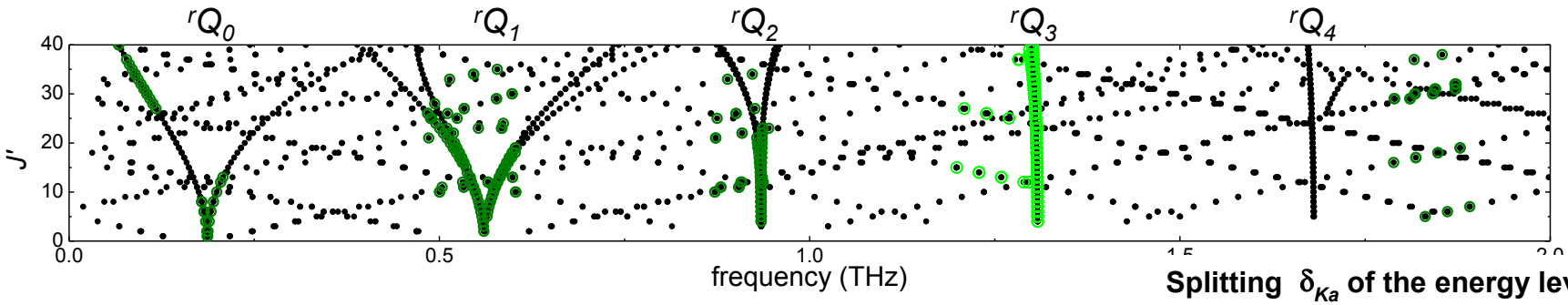
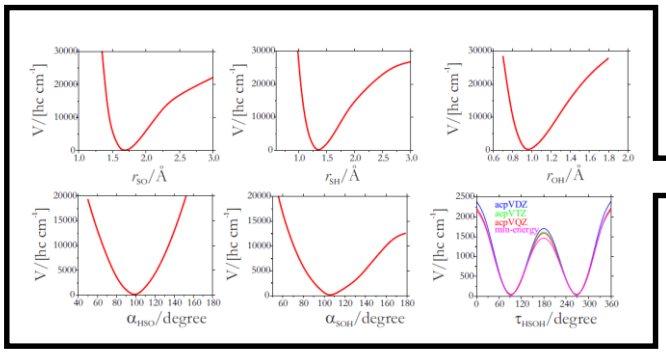
Jon Hougen OSU ´09 RJ01

Torsional splitting



THEORETICAL ROVIBRATIONAL ENERGIES



$$\left(-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2 + V\right)\Psi_{trv} = E_{trv}\Psi_{trv}$$

Yurchenko *et al.*, J. Mol. Spectrosc. (2007)

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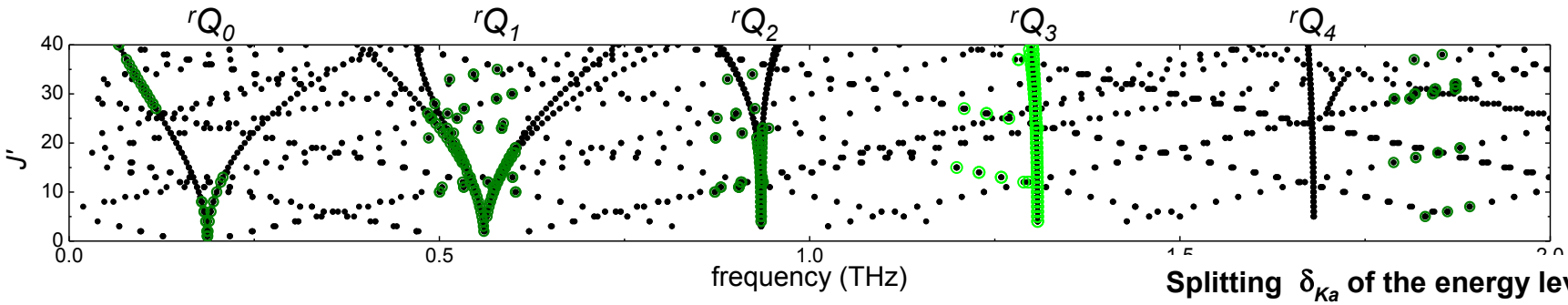
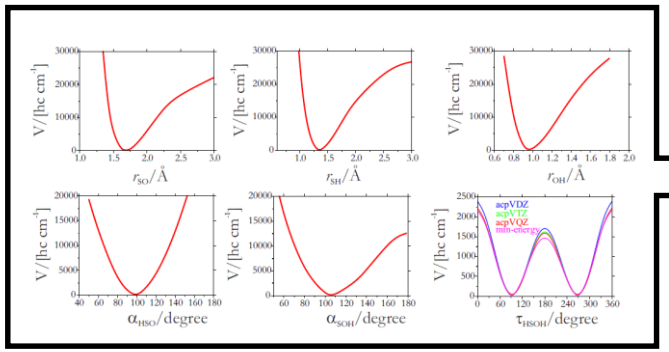
Torsional splitting



THEORETICAL ROVIBRATIONAL ENERGIES



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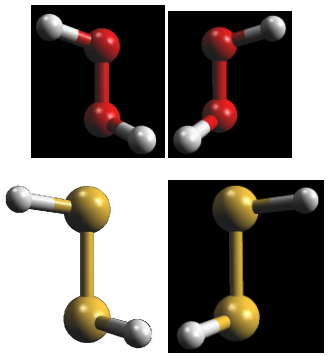
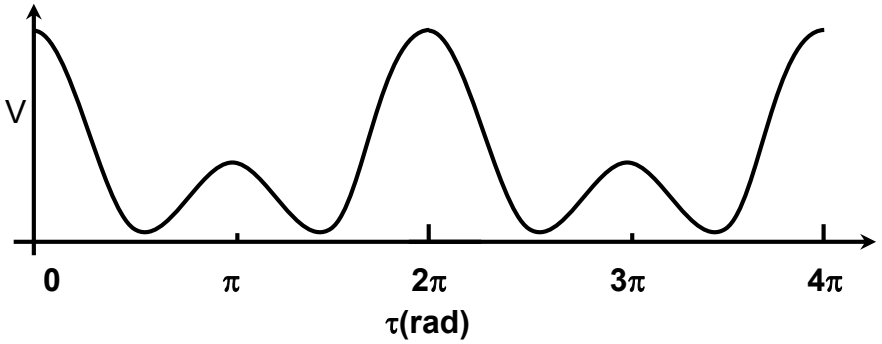
Yurchenko *et al.*, J. Mol. Spectrosc. (2007)

YAMADA – WINNEWISSER – JENSEN MODEL





Hougen and DeKoven, J. Mol. Spectrosc. (1983); Hougen, Can. J. Phys. (1984)

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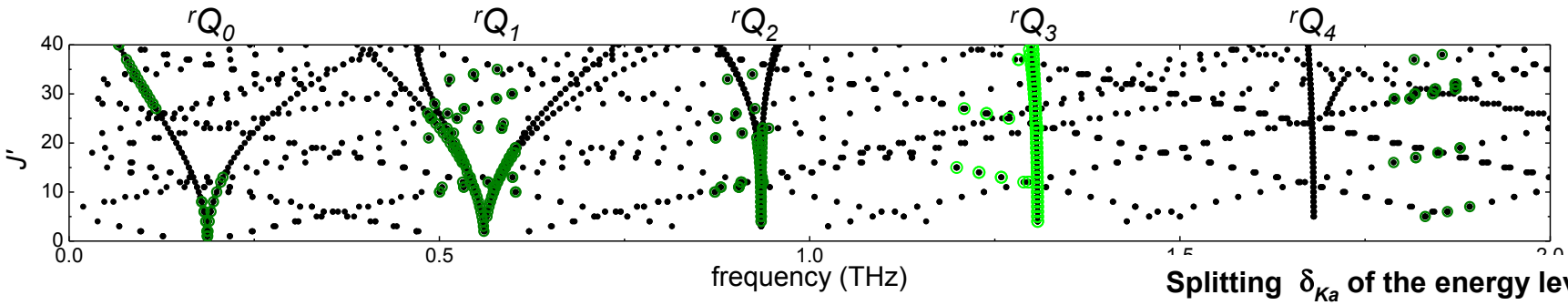
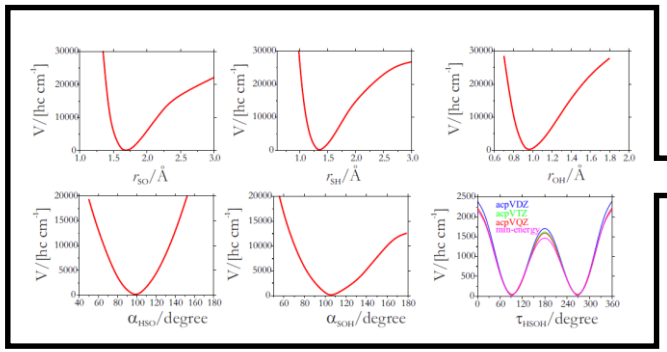
Torsional splitting



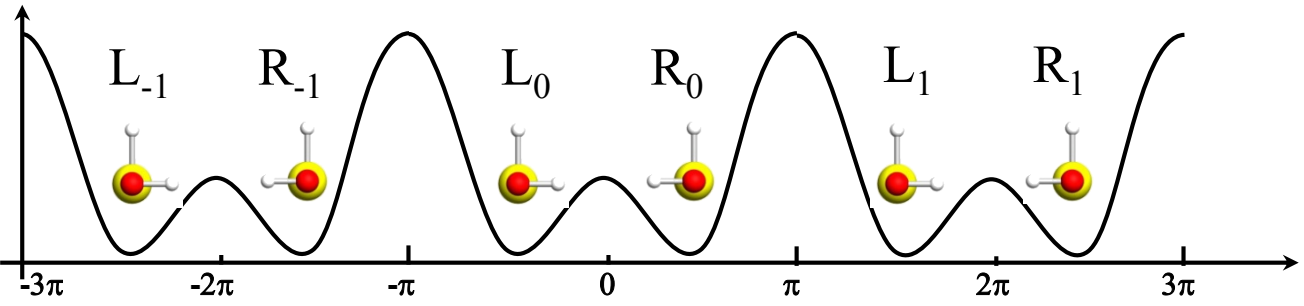
THEORETICAL ROVIBRATIONAL ENERGIES



$$\left(-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2 + V\right)\Psi_{trv} = E_{trv}\Psi_{trv}$$

Yurchenko *et al.*, J. Mol. Spectrosc. (2007)

YAMADA – WINNEWISSER – JENSEN MODEL



Yamada, Winnewisser, and Jensen., J. Mol. Struct. (2004); Yamada *et al.*, J. Mol. Struct (2009)

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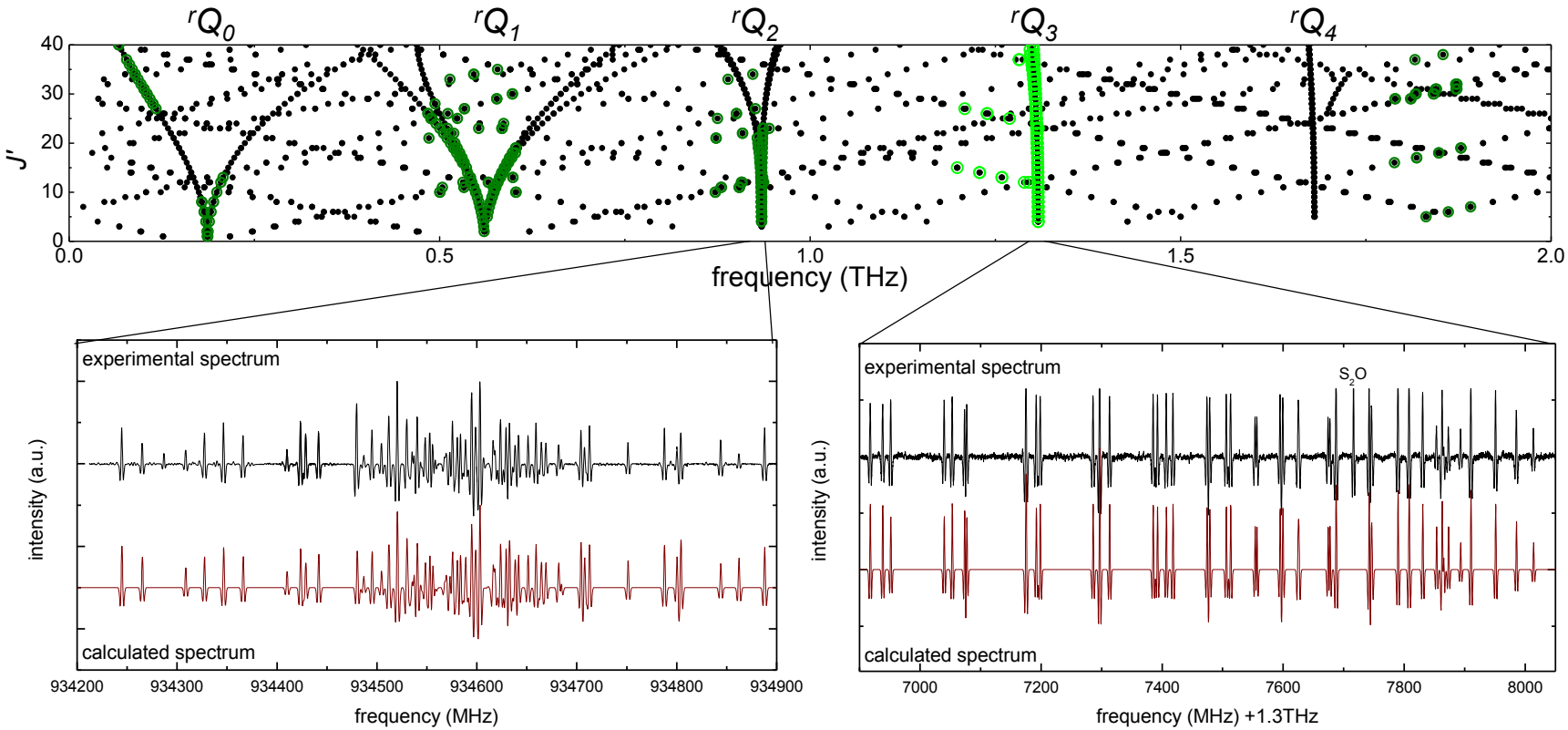
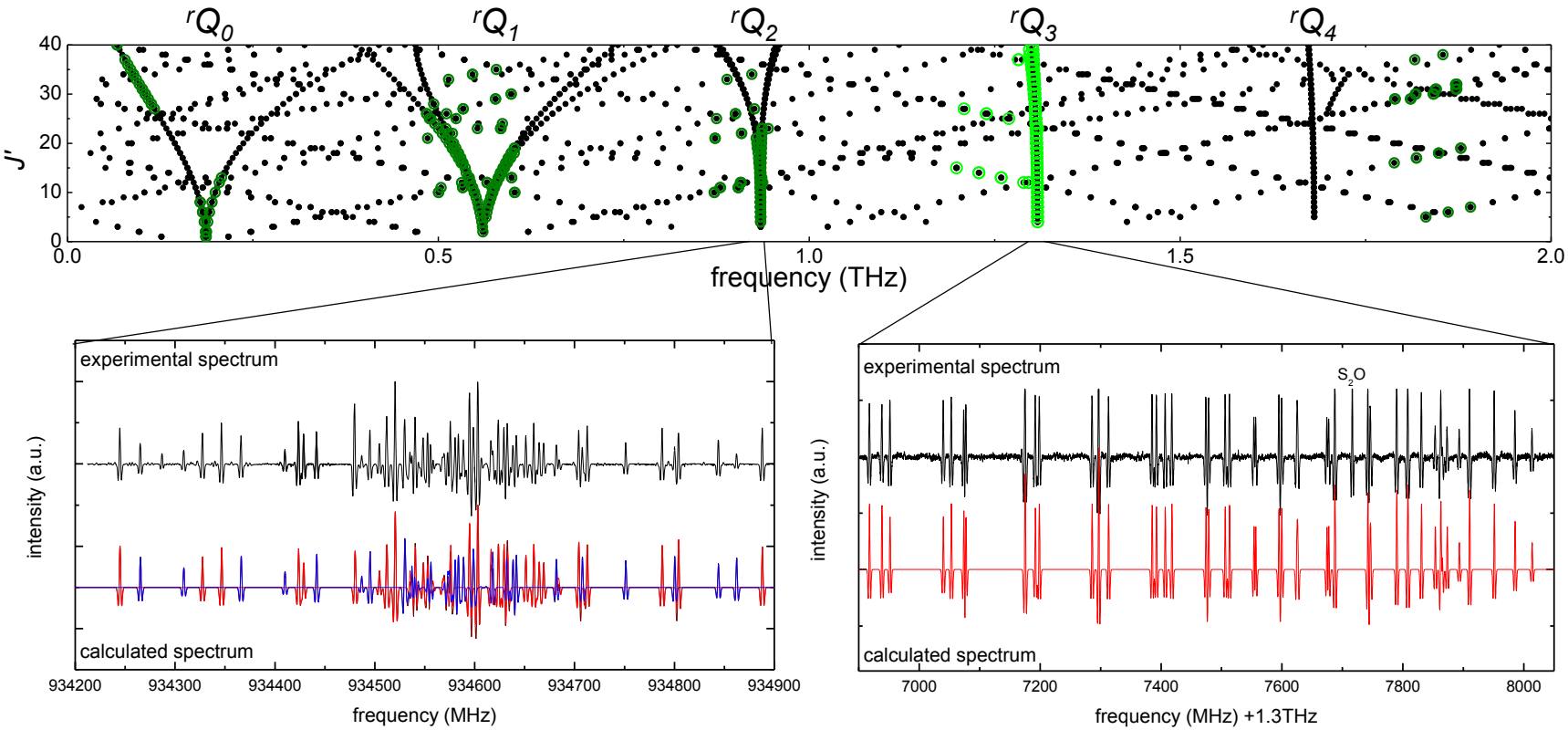
Experimental spectra

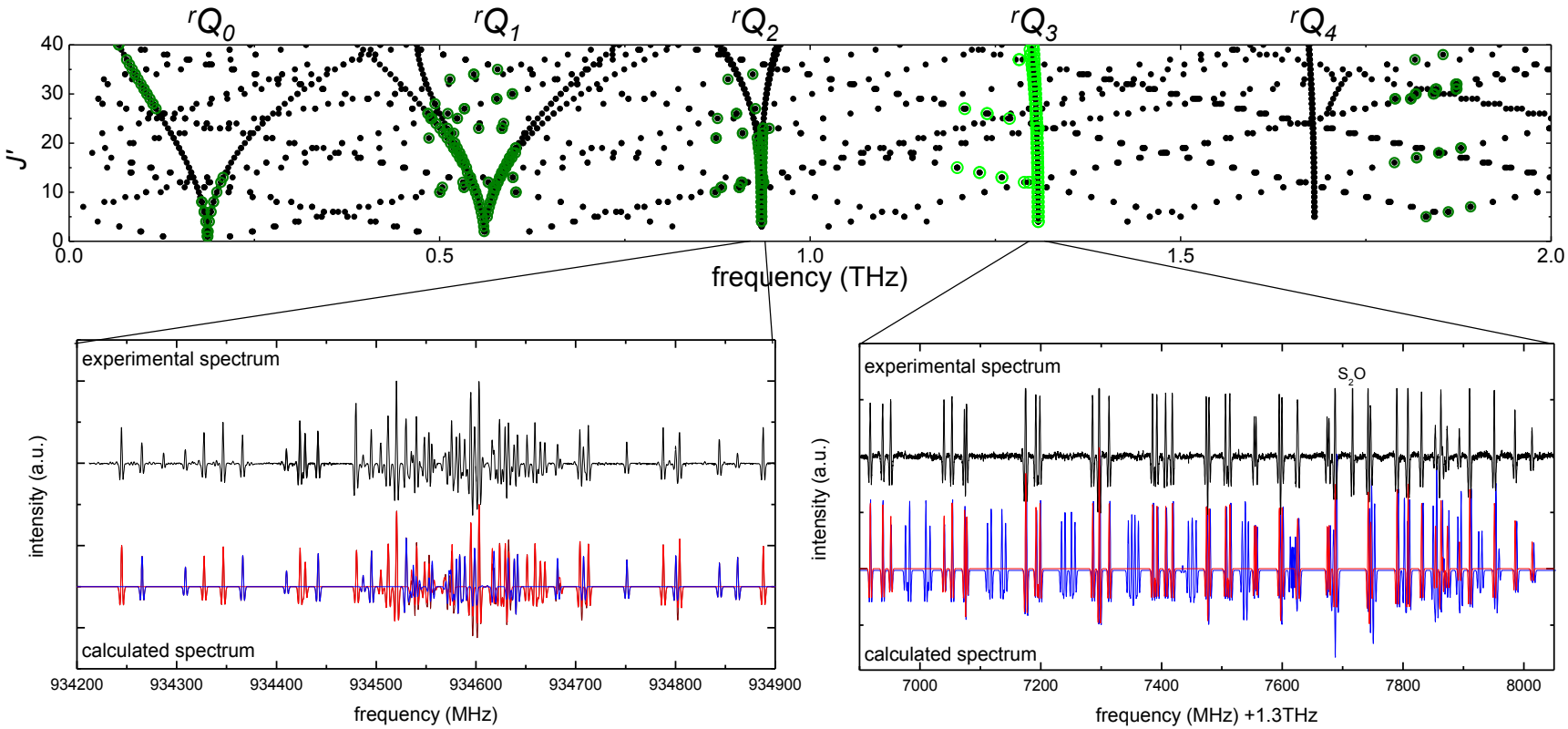


Intensity anomaly



b-, *c*-type

Intensity anomaly



branch	S_b/S_c
$^rQ_0$	0.22(4)
$^rQ_1$	0.23(2)
$^rQ_2$	0.58(11)
$^rQ_3$	< 0.02

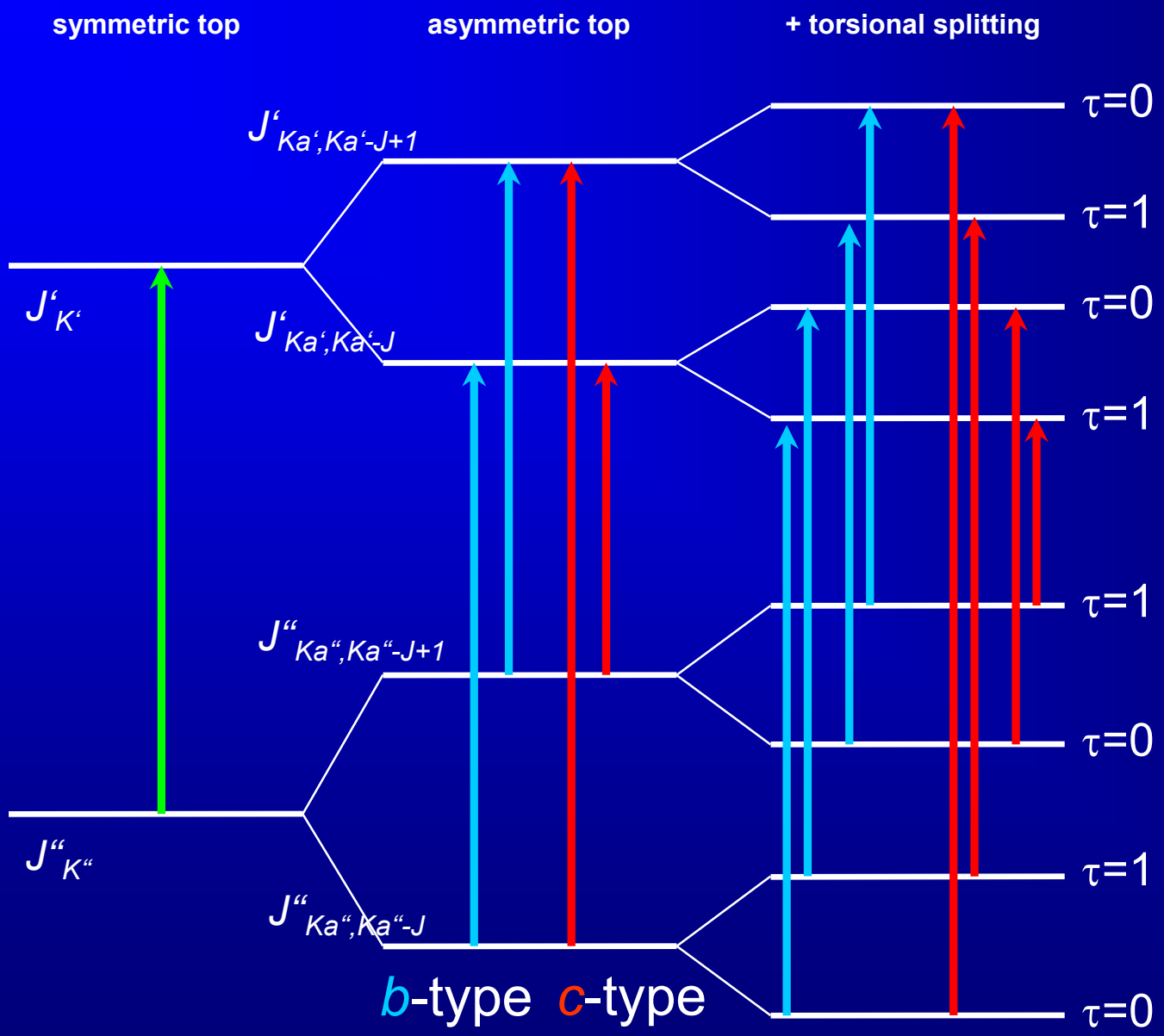
branch	S_b/S_c
$^rP_4$	< 0.02
$^rP_5$	< 0.02
$^rP_6$	< 0.02

Theoretical value: $S_b/S_c=\mu_b^2/\mu_c^2=0.29$

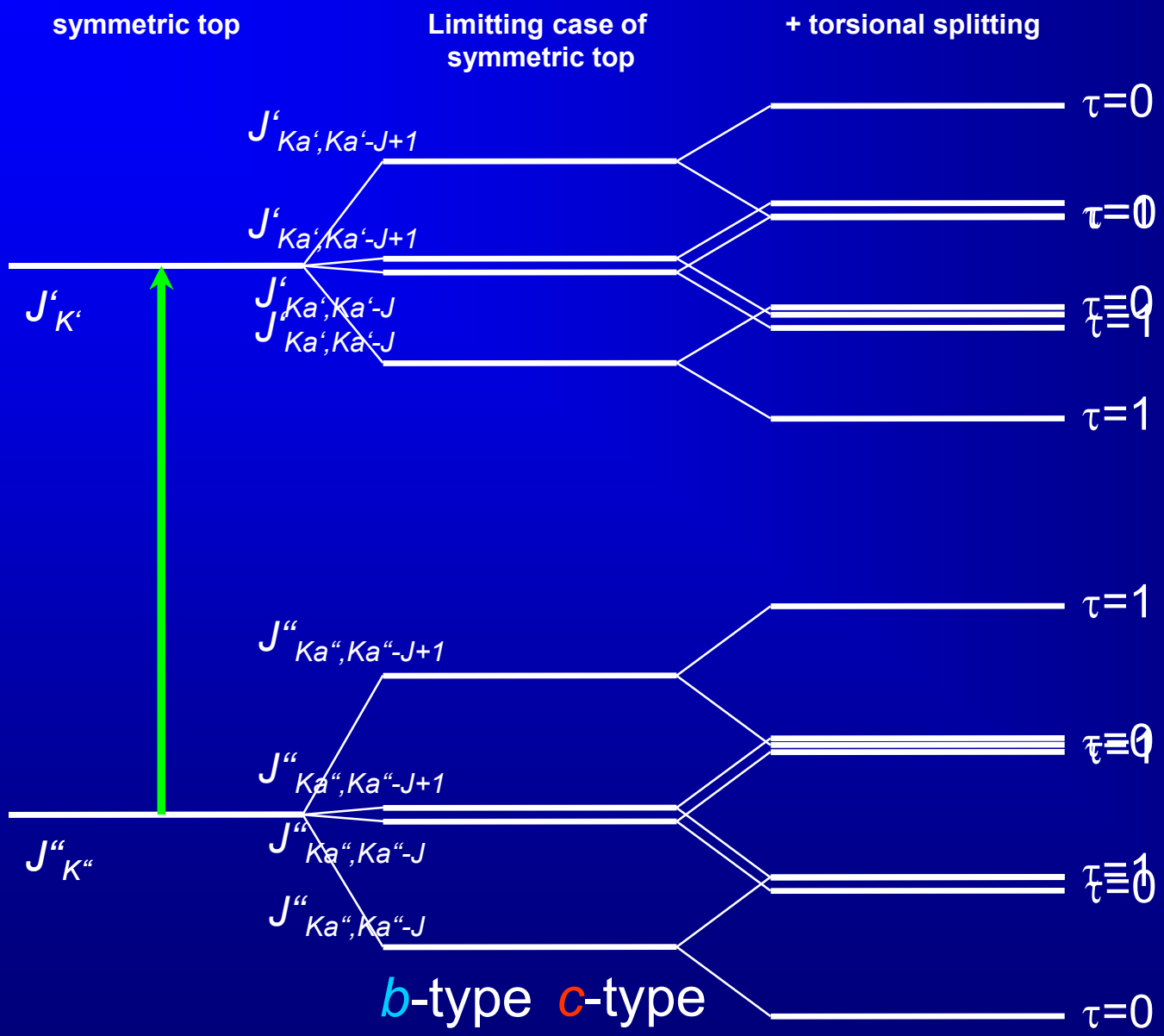
(Winnewisser *et al.*, Chem. Eur. J. (2003))

b-, *c*-type

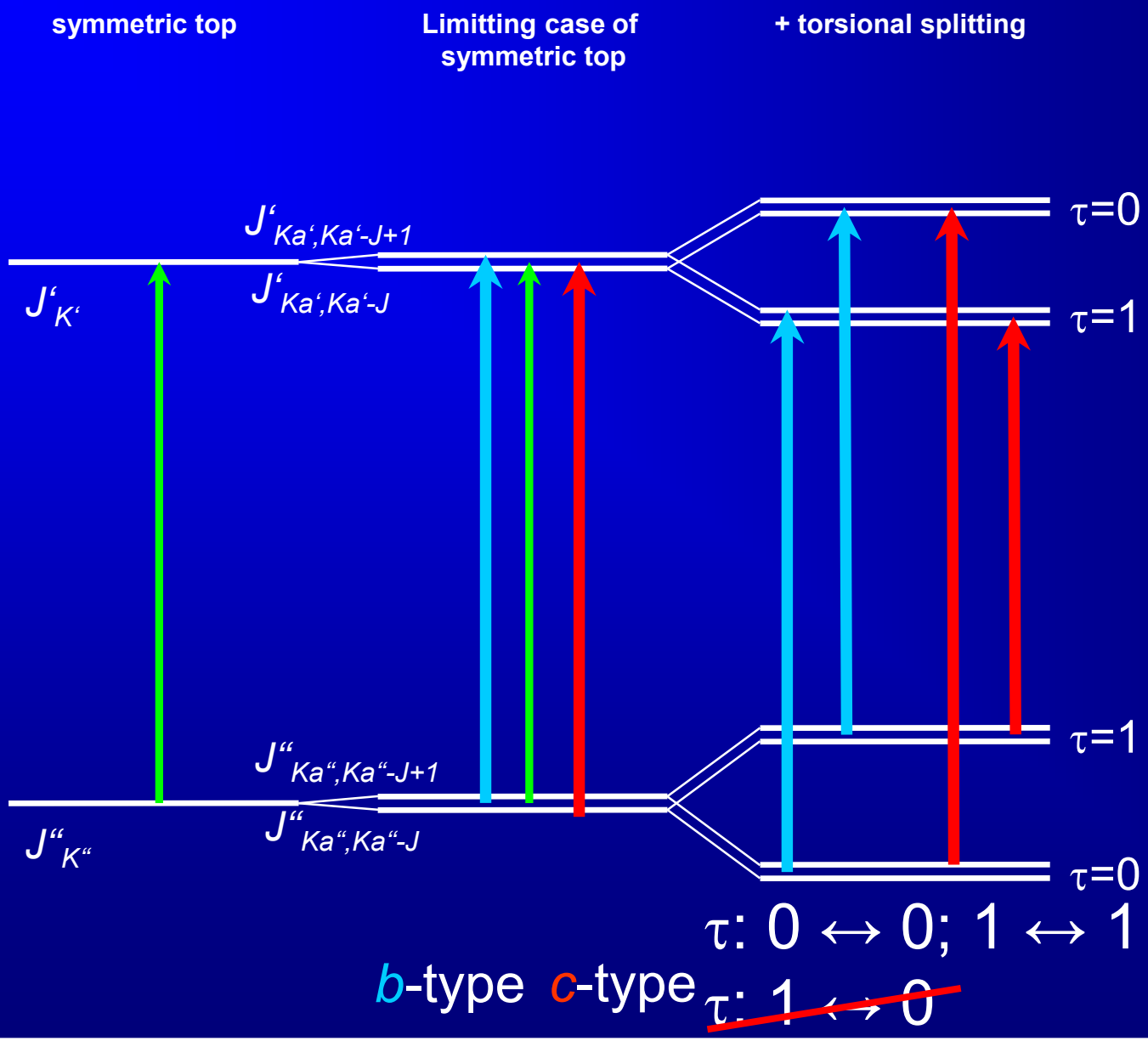
Intensity anomaly



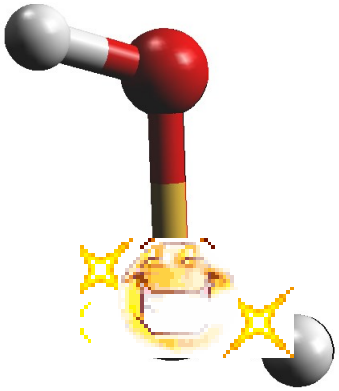
Intensity anomaly

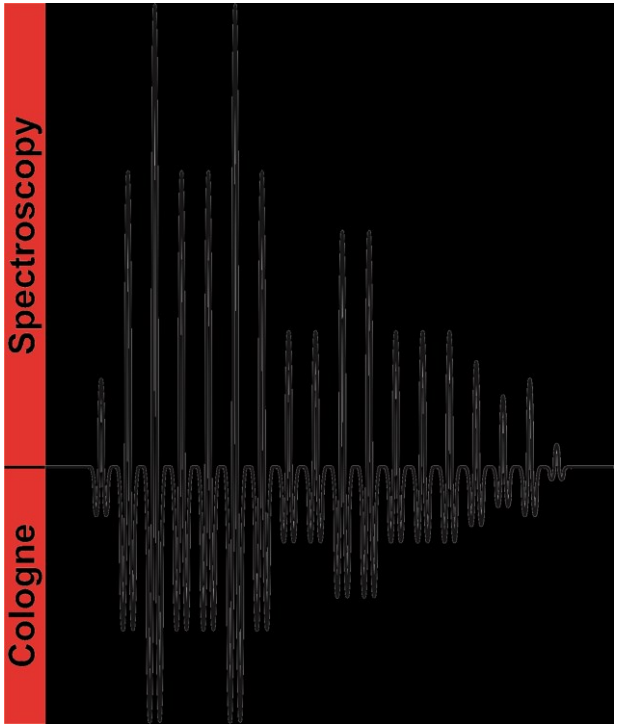


Intensity anomaly

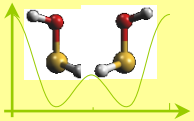


Conclusion



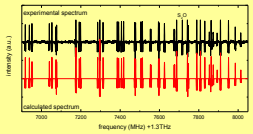


Experimental torsional splittings of HSOH transitions have been recorded up to 2 THz



The new experimental data validate the available theoretical models by Ovsyannikov *et al*. (TROVE) and Yamada *et al*. (YWJ-model)

For K_a" > 2 only pure rotational transitions (*c*-type) have been observed



To Do:

Intensity anomaly:

Special trait of HSOH

vs.

General spectroscopic effect

⇨ Laboratory data of further candidate molecules

⇨ Theoretical model