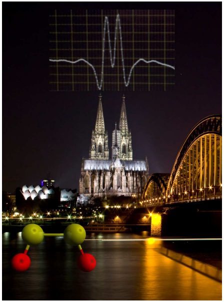
Millimiter-wave spectroscopy of OSSO



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June 16, 2014

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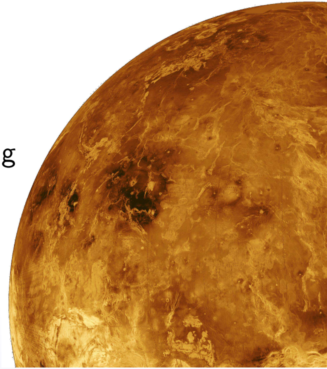
Sulfur-Rich Oxides S_nO_m

Sulfur: element with the largest number of binary oxides[1]
Lower oxides of sulfur: SO, S_2O, S_2O_2, S_3O...

Sulfur containing species in space:

- ∼10 % of known interstellar molecules
- Detected sulfur oxides: SO_2[2], SO[3]
- Observed in molecular clouds, star forming regions, atmospheres (Venus[4], Io)

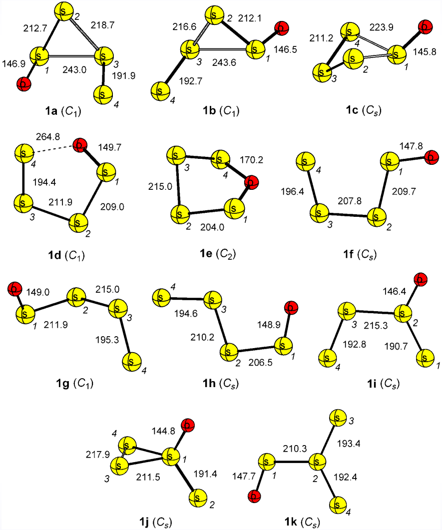


[1] R. Steudel, *Top Curr Chem* **231**, 203 (2003)
[2] L. E. Snyder, *Astrophys. J.* **198**, L81(1975)
[3] C. A. Gottlieb & J. A. Ball, *Astrophys. J.* **184**, L59 (1973)
[4] Image: NASA, http://solarsystem.nasa.gov/planets

Structural complexity of sulfur oxides

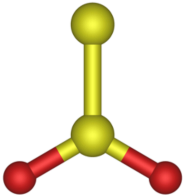
Example: S_4O[1]

- 11 stable conformers
- B3LYP/6-31G(2df)
- Energy within 120 kJ/mol



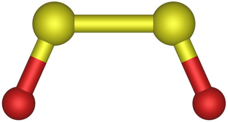
[1] M. W. Wong *et al.*, *Chem. Eur. J.* **13**, 502 (2007)

Disulfur Dioxide, S_2O_2



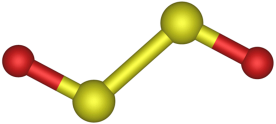
branched

$\mu = 1.31$ D[1]



cis

$\mu = 3.17\ (10)$ D[2]



trans

$\mu = 0$ D

- E(*branched*) < E(*cis*) ∼ E(*trans*)[1]

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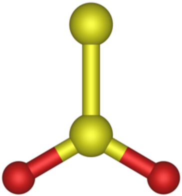
[1] Calculation: CCSD(T)/cc-pwCVQZ

[2] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)

Disulfur Dioxide, S_2O_2



branched

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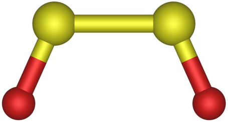

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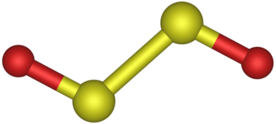
$\mu = 3.17\ (10)$ D[2]



trans

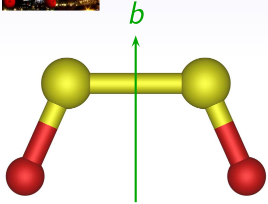
$\mu = 0$ D

- E(*branched*) $<$ E(*cis*) $\sim$ E(*trans*)[1]
- Only the *cis* isomer have been observed to date[2]

[1] Calculation: CCSD(T)/cc-pwCVQZ

[2] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)

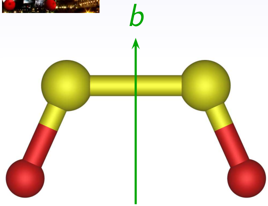
Spectroscopy of OSSO



- planar, C_{2v} symmetry
- b-type transitions
- only levels with $K_a K_c = \text{ee}/\text{oo}$ are populated

[1] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)
[2] S. Thorwirth *et al.*, *J. Mol. Struct.* **795**, 219 (2006)

Spectroscopy of OSSO



- planar, C_{2v} symmetry
- b-type transitions
- only levels with $K_a K_c = \text{ee}/\text{oo}$ are populated

Previous investigations:

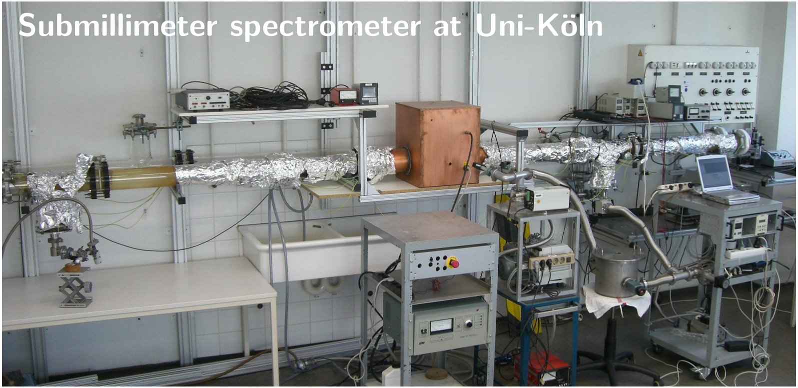
Pure rotational spectroscopy up to 50 GHz[1,2]

- Produced by discharge in SO_2
- OSSO ($\nu = 0$, $\nu_3 = 1$)
- $O^{34}SSO$ ($\nu = 0$)

[1] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)

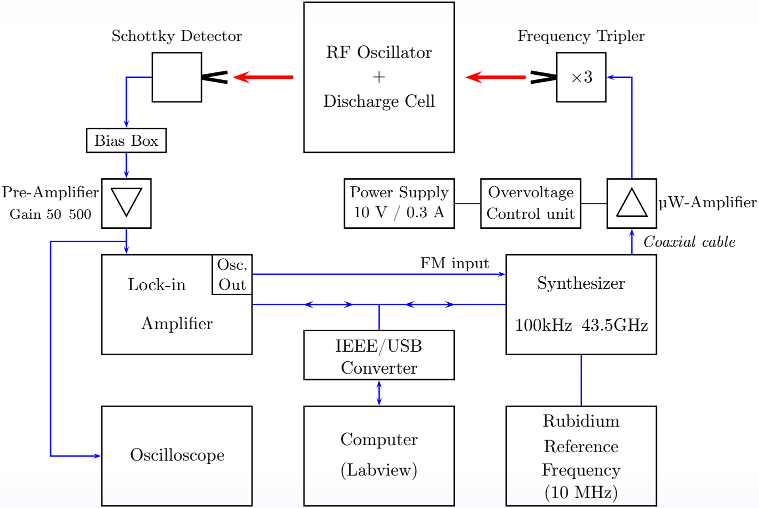
[2] S. Thorwirth *et al.*, *J. Mol. Struct.* **795**, 219 (2006)

Experimental set-up

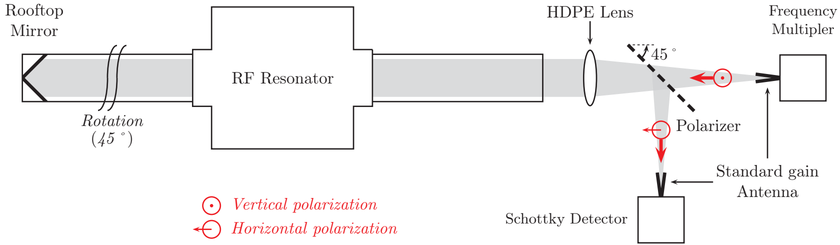


- Frequency multiplication chain (70 GHz – 1.1 THz)
- 5 m long absorption cell
- Radio-frequency (RF) discharge

Electronic configuration

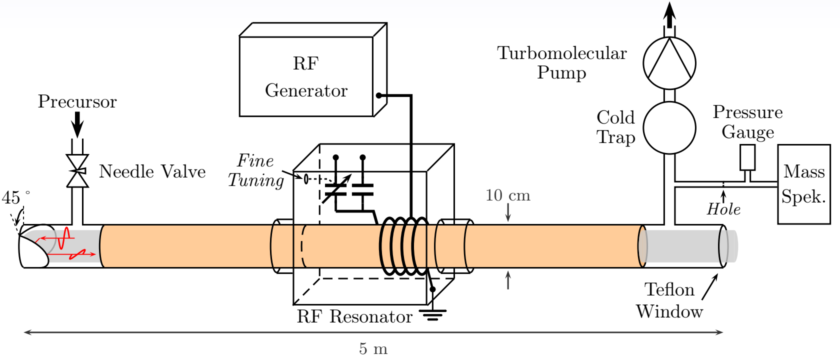


Optical arrangement



- 10 m absorption length

RF-discharge



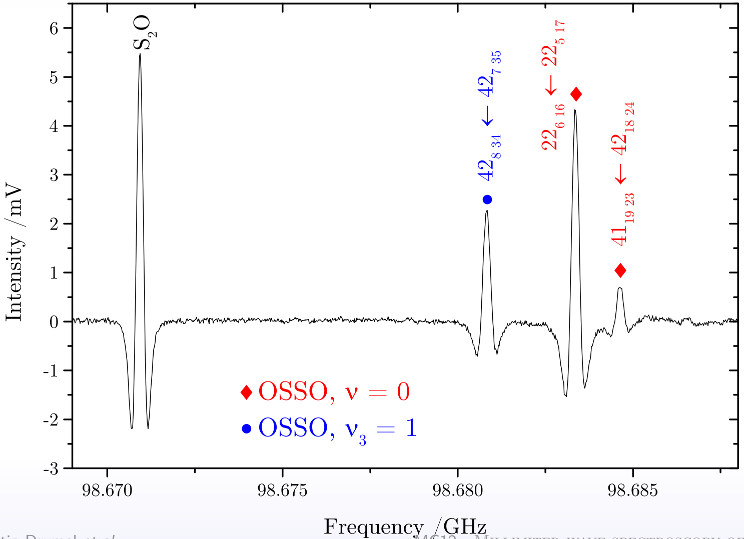
- Precursor: SO_2
- Discharge power: $\leq$ 5W
- Pressure: 3 µbar (flow)

- Other observed species: SO_2 (GS, $\nu_3 = 1$), $SO^{18}O$, $SO^{17}O$, S_2O, SO, ^{34}SO, ^{33}SO, $S^{18}O$

Experimental conditions

- Frequency range covered:
  - 70 – 120 GHz (steps 10 kHz)
  - 340 – 500 GHz (steps 50 kHz)
- 20 ms time constant
- Second harmonic detection

OSSO: ground and $\nu_3 = 1$ states



Results

- 608 lines in the ground state ($J'' \leq 95$, $K_a'' \leq 24$)
  70 – 120 GHz, 340 – 500 GHz
- 156 lines in $\nu_3 = 1$ ($J'' \leq 54$, $K_a'' \leq 12$)
  70 – 120 GHz

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- SNR up to 130, unc. down to 5 kHz

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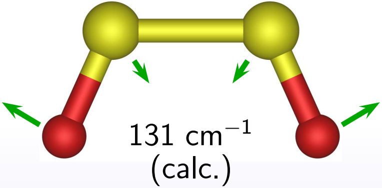
- SNR up to 130, unc. down to 5 kHz
- fc-CCSD(T)/cc-pV(Q+d)Z calculation:
  Vibrationally excited transitions assigned to the ν_3 mode



Frequency and uncertainty

Pseudo-Voigt profile of type $(1-s)G + sL$:

$$y(\nu) = A\left\{(1-s)exp\left[-\ln 2\left(\frac{\nu - B}{C}\right)^2\right] + s\frac{1}{1+\left(\frac{\nu-B}{C}\right)^2}\right\}$$

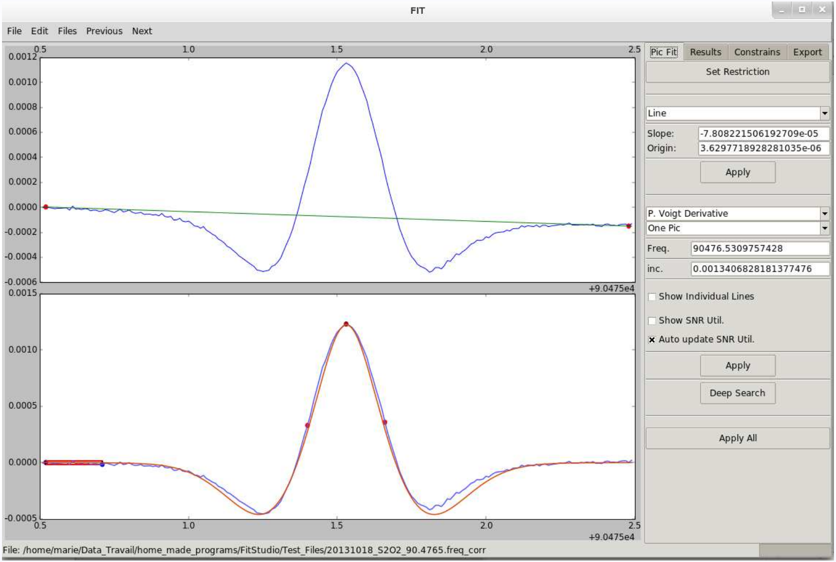
A height of the line, B center frequency, C FWHM, s "shape"

Uncertainty on line frequency[1]:

$$\delta(\nu) = \frac{(C\Delta\nu)^{1/2}}{SNR}\left\{(1-s)\left(\frac{2}{\pi\ln 2}\right)^{1/4} + s\left(\frac{32}{\pi}\right)^{1/2}\right\}$$

[1] D. Landman *et al.*, *Astrophys. J.* **261**, 732 (1982)

Frequency and uncertainty



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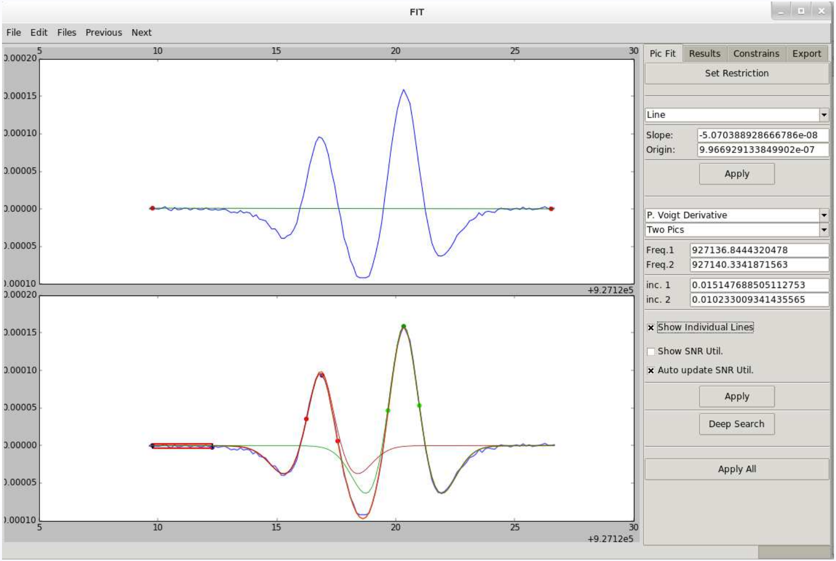

Fits

Watson-A reduction with SPFIT/SPCAT programs[1]

GS	$\nu_3 = 1$
74 lines – literature[2,3]	20 lines – literature[2]
608 lines – this work	156 lines – this work

[1] H. M. Pickett, *J. Mol. Spectrosc.* **148**, 371 (1991)

[2] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)

[3] S. Thorwirth *et al.*, *J. Mol. Struct.* **795**, 219 (2006)

Fits

Watson-*A* reduction with SPFIT/SPCAT programs[1]

GS

- 74 lines – literature[2,3]
- 608 lines – this work
- RMS= 40 kHz (our data: 23 kHz)
- $\sigma = 0.99$

$\boldsymbol{\nu_3 = 1}$

- 20 lines – literature[2]
- 156 lines – this work
- RMS= 50 kHz (our data: 7 kHz)
- $\sigma = 1.04$

[1] H. M. Pickett, *J. Mol. Spectrosc.* **148**, 371 (1991)

[2] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)

[3] S. Thorwirth *et al.*, *J. Mol. Struct.* **795**, 219 (2006)

Molecular parameters: GS and $\nu_3 = 1$

Parameter	$\nu = 0$		$\nu_3 = 1$	
(MHz)	This work	S. Thorwirth (2006)	This work	F. J. Lovas (1974)
A	12972.92980 (10)	12972.93037 (72)	13133.21612 (45)	13133.245 (22)
B	3488.970410 (34)	3488.96986 (33)	3469.568432 (77)	3469.5754 (62)
C	2745.054829 (31)	2745.05543 (20)	2736.199454 (72)	2736.2036 (77)
$\Delta_J \times 10^3$	3.380639 (20)	3.3717 (44)	3.180504 (79)	3.125 (45)
$\Delta_{JK} \times 10^3$	-26.97455 (14)	-26.926 (35)	-26.5592 (13)	-26.07 (39)
$\Delta_K \times 10^3$	97.04625 (57)	96.921 (38)	104.136 (15)	98.7 (46)
$\delta_J \times 10^3$	1.0308574 (72)	1.0313 (17)	0.957989 (25)	0.9662 (80)
$\delta_K \times 10^3$	6.50171 (27)	6.158 (83)	6.64716 (87)	6.21 (39)
$\Phi_J \times 10^9$	0.3703 (49)	13.9 (24)		
$\Phi_{JK} \times 10^6$	0.16598 (12)	0.087 (30)	0.1621 (17)	
$\Phi_{KJ} \times 10^6$	-1.92136 (48)	-0.89 (15)	-1.985 (31)	
$\Phi_K \times 10^6$	5.6180 (16)	3.51 (43)	6.74 (37)	
$\phi_J \times 10^9$	0.4595 (23)	-11.5 (11)	0.320 (19)	
$\phi_{JK} \times 10^6$	-0.01177 (10)		-0.0159 (14)	
$\phi_K \times 10^6$	0.7542 (25)		0.755 (32)	
$L_J \times 10^{12}$	0.06273 (43)			
$L_{JJK} \times 10^{12}$	-0.182 (18)			
$L_{JK} \times 10^9$	-0.02326 (46)			
$L_{KKJ} \times 10^9$	0.1688 (14)		-1.00 (17)	
$L_K \times 10^9$	-0.4099 (15)		7.7 (18)	
$l_J \times 10^{12}$	0.02917 (22)			
$l_{JK} \times 10^{12}$	0.295 (12)			
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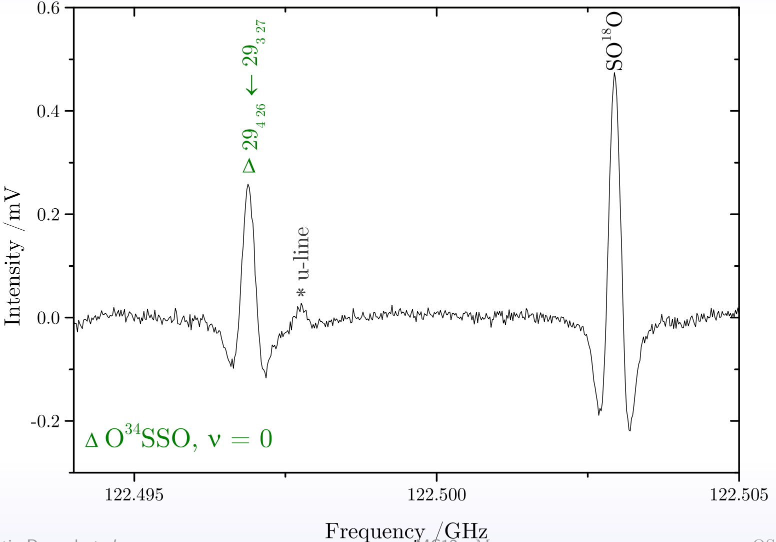
$O^{34}SSO$


0.6
0.4
0.2
0.0
-0.2
Intensity /mV
Δ $29_{4\,26} \leftarrow 29_{3\,27}$
$SO^{18}O$
* u-line
Δ $O^{34}SSO$, $\nu = 0$
122.495
122.500
122.505
Frequency /GHz

Fit

Watson-*A* reduction with SPFIT/SPCAT programs[1]

- 19 lines – literature[2]
- 58 lines – this work (70 – 120 GHz)
- RMS= 72 kHz (our data: 17 kHz)
- $\sigma = 1.03$

[1] H. M. Pickett, *J. Mol. Spectrosc.* **148**, 371 (1991)

[2] F. J. Lovas *et al.*, *J. Chem. Phys.* **60**, 5005 (1974)

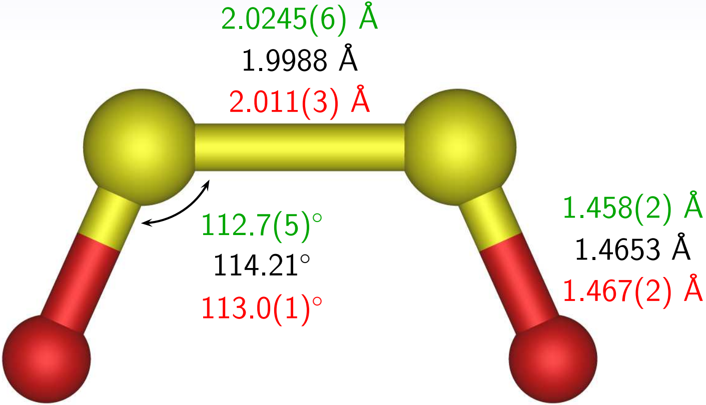
Molecular parameters of $O^{34}SSO$

Parameter	This work	F. J. Lovas (1974)
A	12845.6535 (42)	12845.671 (28)
B	3441.42831 (65)	3441.439 (16)
C	2709.90814 (62)	2709.911 (13)
$\Delta_J \times 10^3$	3.21332 (89)	3.210 (96)
$\Delta_{JK} \times 10^3$	-25.7457 (62)	-25.30 (44)
$\Delta_K \times 10^3$	94.80 (14)	89.8 (60)
$\delta_J \times 10^3$	0.978236 (86)	0.9884 (97)
$\delta_K \times 10^3$	6.2498 (43)	5.85 (43)
$\Phi_{JK} \times 10^6$	0.1026 (56)	
$\Phi_{KJ} \times 10^6$	-1.74 (22)	
$\Phi_K \times 10^6$	8.0 (24)	

Molecular parameters of $O^{34}SSO$

Parameter	This work	F. J. Lovas (1974)
A	12845.6535 (42)	12845.671 (28)
B	3441.42831 (65)	3441.439 (16)
C	2709.90814 (62)	2709.911 (13)
$\Delta_J \times 10^3$	3.21332 (89)	3.210 (96)
$\Delta_{JK} \times 10^3$	-25.7457 (62)	-25.30 (44)
$\Delta_K \times 10^3$	94.80 (14)	89.8 (60)
$\delta_J \times 10^3$	0.978236 (86)	0.9884 (97)
$\delta_K \times 10^3$	6.2498 (43)	5.85 (43)
$\Phi_{JK} \times 10^6$	0.1026 (56)	
$\Phi_{KJ} \times 10^6$	-1.74 (22)	
$\Phi_K \times 10^6$	8.0 (24)	

Geometry of OSSO



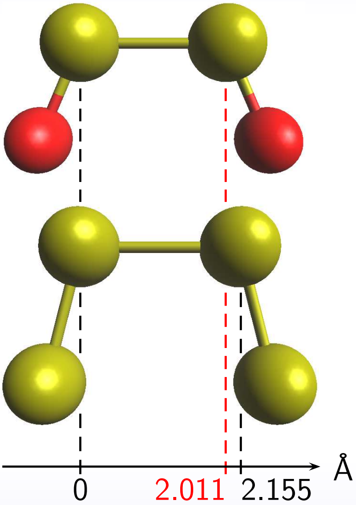
Empirical, F. J. Lovas *et al.* (1974)

Calculated, CCSD(T)/cc-pwCVQZ

Empirical, this work, using zero-point vibrational corrections calculated at CCSD(T)/cc-pV(Q+d)Z

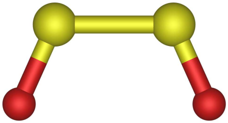
Geometry of OSSO

S-S bond length:
about 7 % shorter
than in isovalent S_4[1]



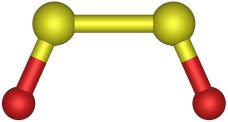
[1] S. Thorwirth *et al.*, *J. Chem. Phys.* **123**, 054326 (2005)

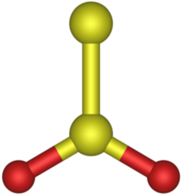
Prospects



- ***cis*-OSSO**
  - Improved structure
    → other isotopologues (FTMW)
  - ν_3 band center:
    beamtime accepted at SOLEIL synchrotron

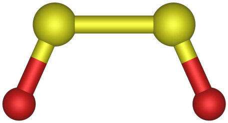
Prospects

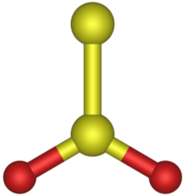


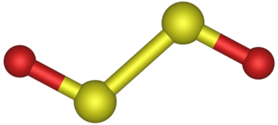


- ***cis*-OSSO**
  - Improved structure
    → other isotopologues (FTMW)
  - ν_3 band center:
    beamtime accepted at SOLEIL synchrotron
- ***branched*-S_2O_2**
  - Pure rotation
    → Chirped-pulse + FTMW
    (see talk RE03)
  - HR ro-vibration (SOLEIL)

Prospects

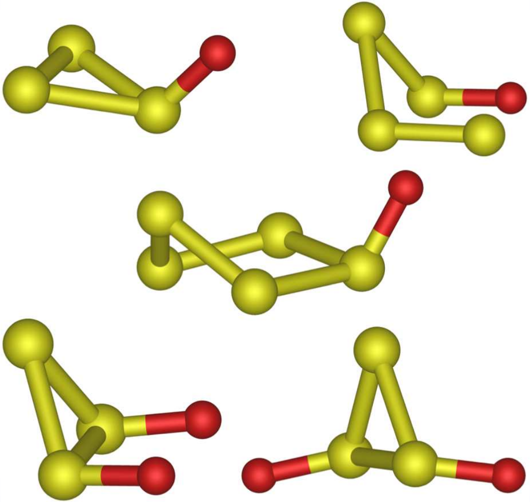




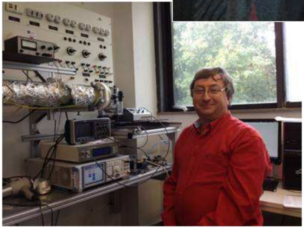


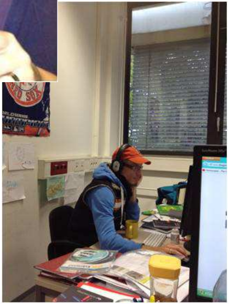
- ***cis*-OSSO**
  - Improved structure
    → other isotopologues (FTMW)
  - ν_3 band center:
    beamtime accepted at SOLEIL synchrotron
- ***branched*-S_2O_2**
  - Pure rotation
    → Chirped-pulse + FTMW
    (see talk RE03)
  - HR ro-vibration (SOLEIL)
- ***trans*-OSSO** ($\mu = 0$)
  - HR ro-vibration (SOLEIL)

Other lower oxides of sulfur



Acknowledgements





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