THE ROTATIONAL SPECTRUM OF *CIS*- AND *TRANS*-HSSOH

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In this talk we present the first pure rotational lines of Oxatrisulfane, HSSOH. Oxatrisulfane is one link between the well-known skew chain molecules HSSSH and HOOOH. The structure of trisulfane HSSSH has been determined using rotational spectroscopy by Liedke *et al.*[a] showing HSSSH to form two stable conformers, *trans* and *cis*, with the *trans*-conformer to be slightly more stable. Only recently hydrogen-trioxide HOOOH has been discovered by Suma *et al.*[b] observing the rotational spectra of the *trans* conformer. For this molecule no evidence for the *cis* structure has been found.
First experimental evidence for the formation of HSSOH was given by Königshofen *et al.*[c] via flash vacuum pyrolysis of t-BuS(O)St-Bu at T $> 700^{\circ}$C using IR-spectroscopy to monitor the pyrolysis products. We employed this method to synthesize HSSOH and performed first high-resolution millimeterwave measurements in the range of 75–120 GHz by introducing an all solid state spectrometer. More than 170 lines of the *cis* conformer and more than 30 lines of *trans*-HSSOH have been undoubtly identified. Both conformeres are close to the limiting case of a prolate symmetric top with $\kappa_{cis} = -0.925$ and $\kappa_{trans} = -0.924$ respectively. Their permanent dipole moment points mainly along the *b*- and *c*- principle axes and therefore the spectrum displays a clear perpendicular structure. For analyzing the identified lines a standard *S*-reduced Hamiltonian has been used and we were able to fit the rotational parameters A, B, C as well as the centrifugal distortion parameters D_J, D_{JK}, D_K, d_1 and d_2. The *c*-type transitions of *cis*-HSSOH are approx. 14 times more intense than the corresponding *b*-type transitions, whereas in case of *trans*-HSSOH the intensities of the *b*- and *c*-type transitions are almost equal. All experimentally derived parameters are in excellent agreement with those obtained by high level ab initio calculations[d].

[a] Liedtke *et al.*, *J. Mol. Struct.* **413** 265–270 (1997)
[b] Suma *et al.*, *JACS* **127** 14998–14999 (2005)
[c] Königshofen *et al.*, *Z. Anorg. Allg. Chem.* **625** 1779–1786 (1999)
[d] J. Gauss, private communication