

Detection of HSNO, a crucial intermediate linking NO and H₂S chemistries

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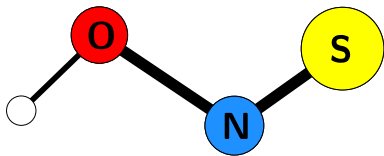
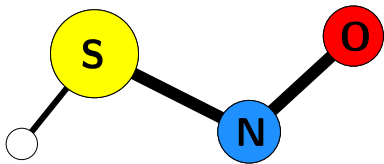
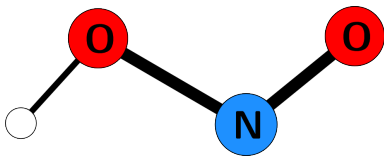
³Department of Chemistry, University of California-Davis, CA, USA

⁴Department of Chemistry, MIT, Cambridge, MA, USA

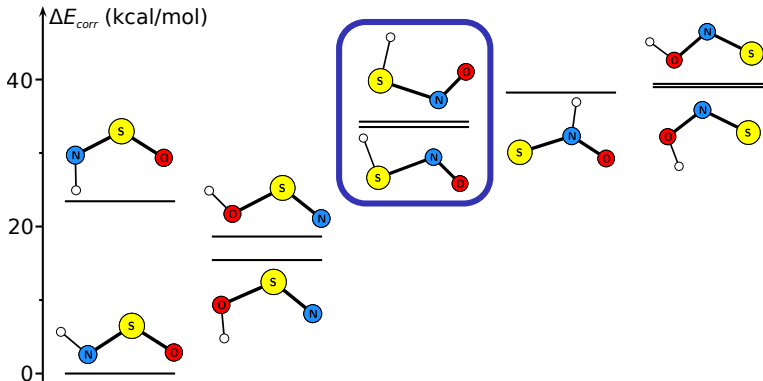
⁵I. Physikalisches Institut, Universität zu Köln, Germany



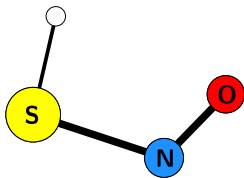
Little is known on sulfur analogs
of nitrous acid



Thionitrous acid, HSNO , is
a metastable isomer of *cis*- HNSO

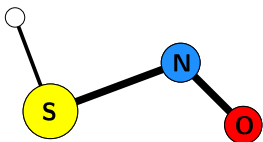


HSNO is an elusive molecule



Biologically relevant species

- S-nitrosothiol (RSNO)
- potential NO carrier
- potential product of the *in vivo* 'cross-talk' between H₂S and NO



Inconclusive theoretical studies

Experimental investigation limited to argon matrices

Detection of HSNO, a crucial intermediate linking NO and H₂S chemistries

Investigation of the
microwave spectrum of HSNO

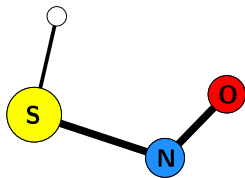
Accurate determination
of its geometry

HSNO is a product of the reaction
between H_2S and NO

Formed from H_2S and NO
high concentration
no discharge

The gas phase reaction:
 $\text{H}_2\text{S} + \text{NO} \rightarrow \dots \rightarrow \text{HSNO}$
is endothermic
 $\sim + 60 \text{ kcal/mol}$

Detection of HSNO, a crucial intermediate linking NO and H₂S chemistries



FT-MW and DR measurements

Pure rotational transitions

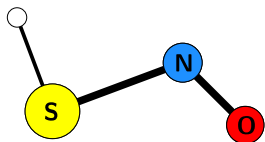
4 isotopologues

Semi-experimental geometrical determination

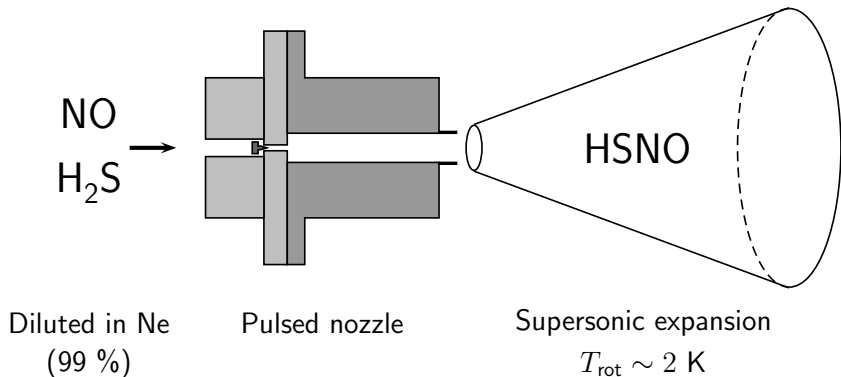
Elongated S-N bond

Insights into HSNO formation

N₂O₃ reaction partner



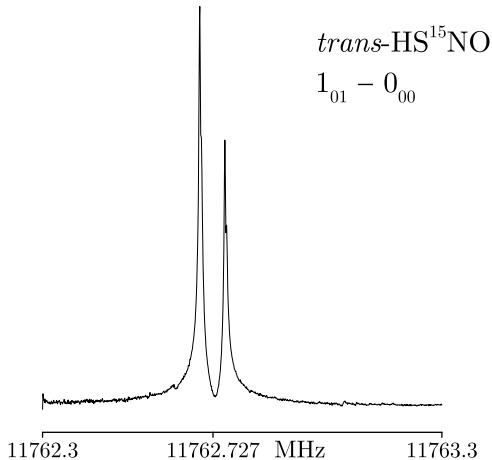
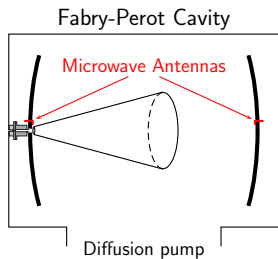
HSNO is readily formed from H_2S and NO in our gas experiment



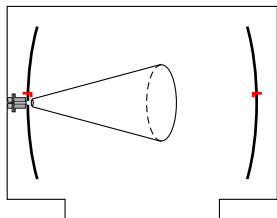
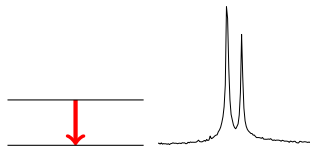
NO DISCHARGE

DSNO, H^{34}SNO , HS^{15}NO

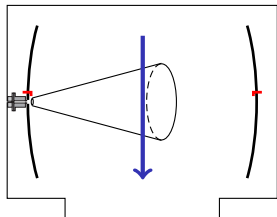
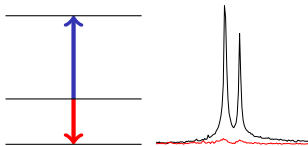
Accurate frequencies have been measured using FT-MW spectroscopy up to 40 GHz



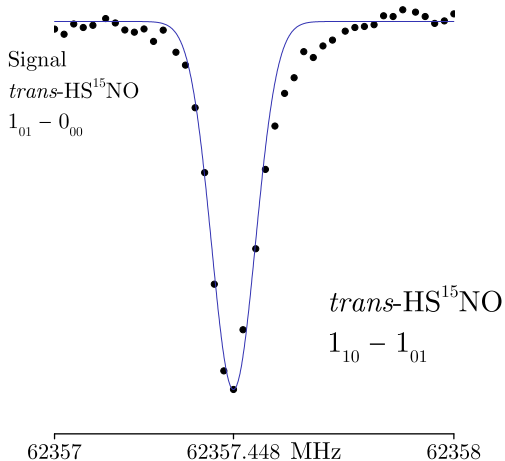
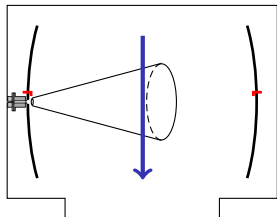
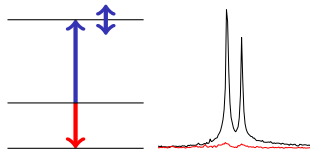
Observations have been extended up to 90 GHz using double-resonance



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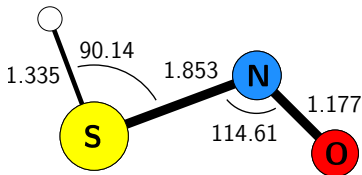
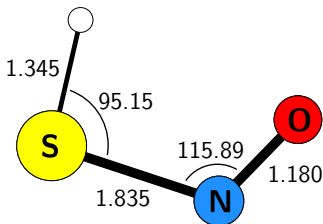
Observations have been extended up to 90 GHz using double-resonance



The derived semi-experimental structure reveals an elongated S–N bond

S–N bond length

- HSNO: $\sim 1.84 \text{ \AA}$
- typical: $\sim 1.7 \text{ \AA}$

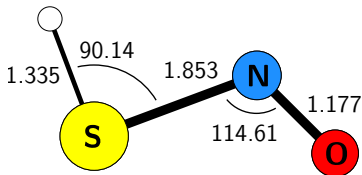
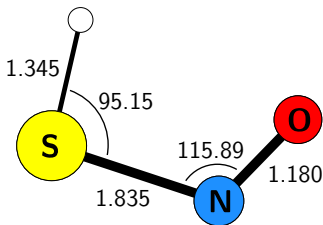
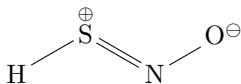
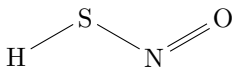


Quantum-chemical calculations: CCSD(T)/cc-pV(Q+d)Z

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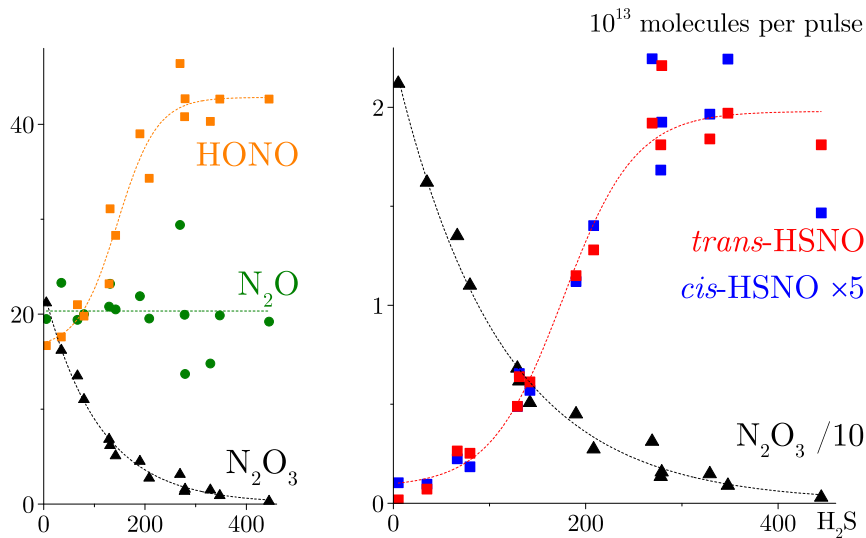
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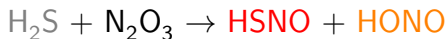
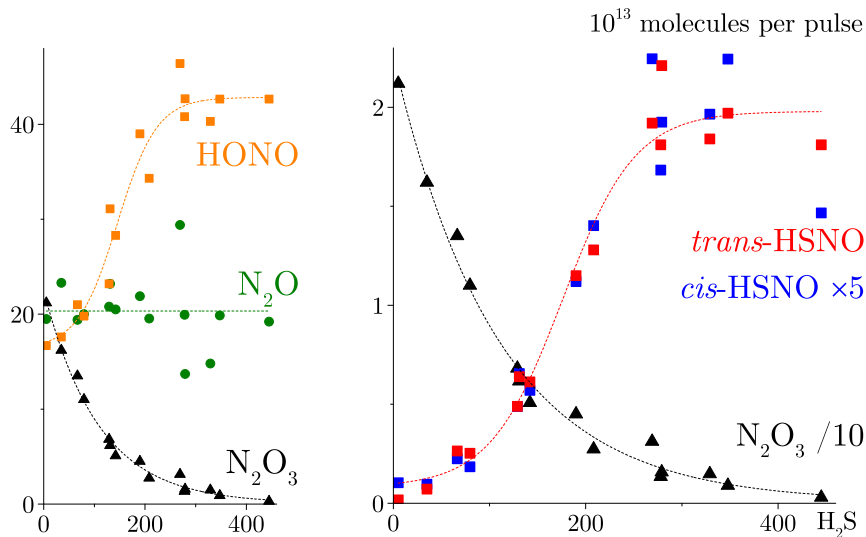


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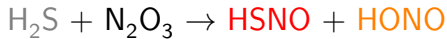
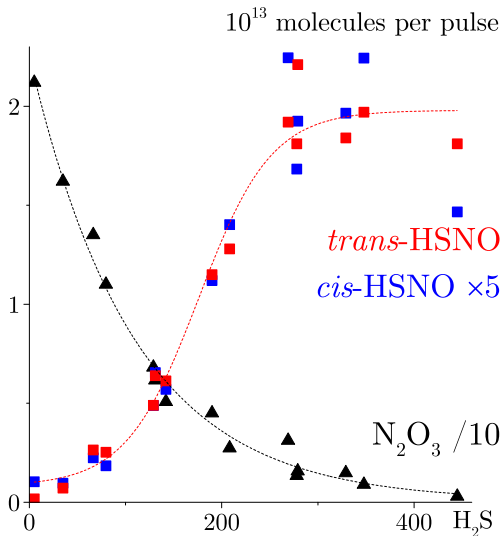
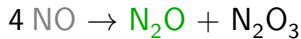
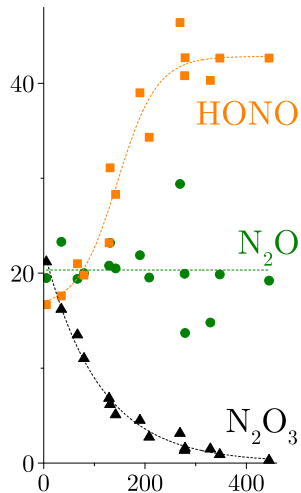
N_2O_3 is a key reaction partner



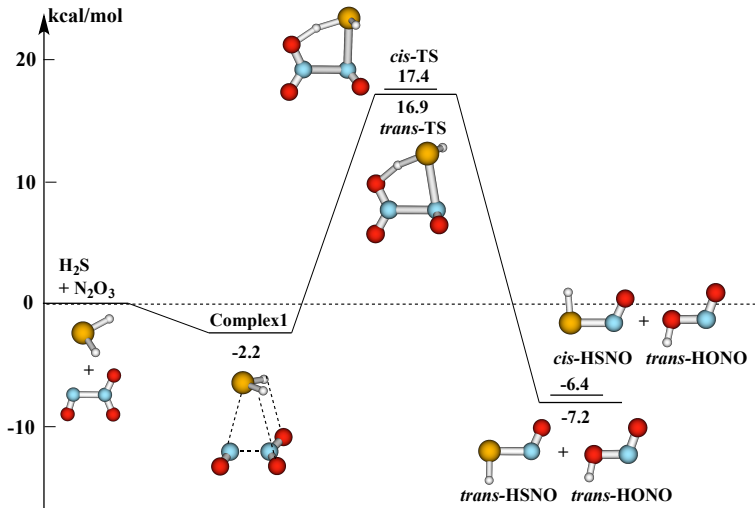
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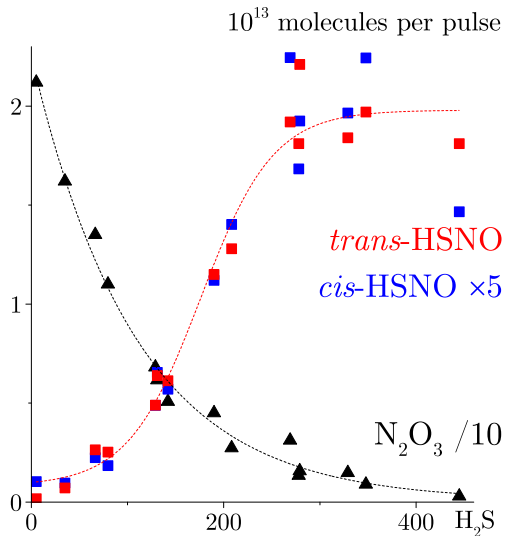
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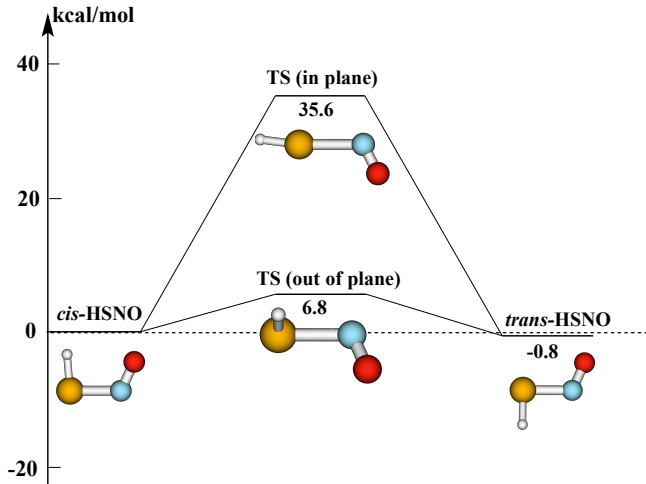
The production of HSNO via N_2O_3 is exothermic



trans-HSNO is 5 times more abundant than the *cis* form



The *cis* – *trans* isomerization faces a high barrier



Detection of HSNO, a crucial intermediate linking NO and H₂S chemistries

Pure rotational transitions
up to 90 GHz

Accurate structure
elongated S–N bond

Formed via surface reactions
involving N₂O₃

Detection of HSNO, a crucial intermediate linking NO and H₂S chemistries

Candidate for
astronomical detection

[H, S, N, O]

dipole \sim 1 D

Theoretical benchmark

Detection of HSNO, a crucial intermediate linking NO and H₂S chemistries

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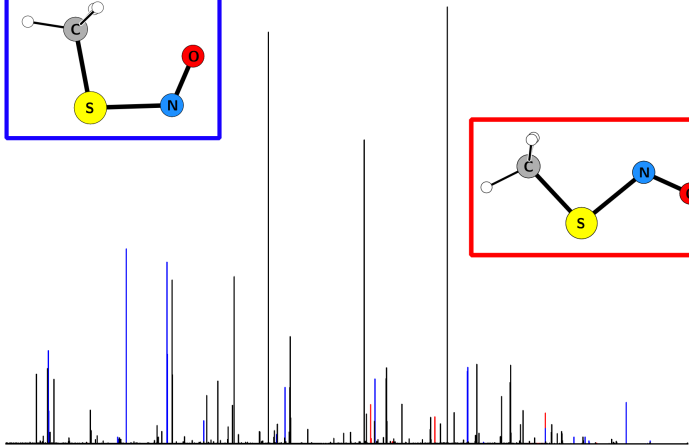
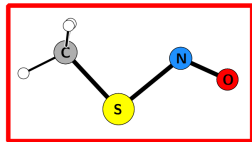
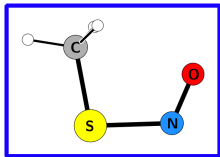
[H, S, N, O]

dipole ~ 1 D

Theoretical benchmark

Are larger RSNOs formed
from RSH in a similar way?

Preliminary investigations of the $\text{CH}_3\text{SH} + \text{NO}$ reaction reveal CH_3SNO



Chirped-pulse spectrum 8–18 GHz

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