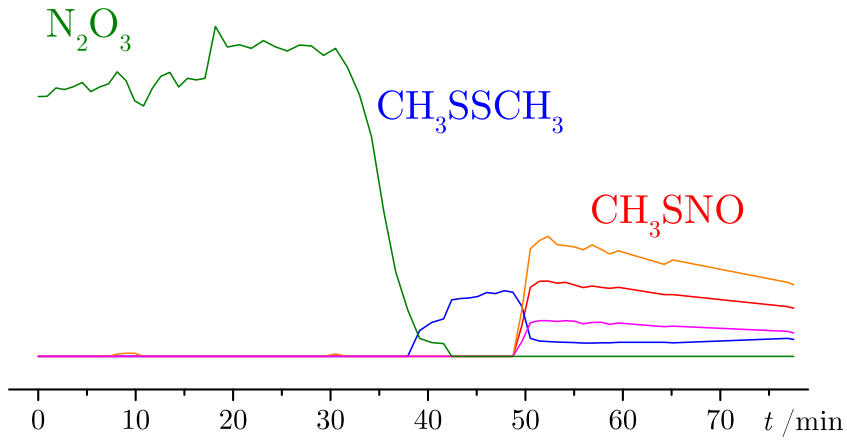
Probing the $CH_3SH + N_2O_3$ reaction by automated microwave double resonance spectroscopy



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Two key questions from HSNO study

- Can the reaction $H_2S + N_2O_3 \rightarrow HSNO + HONO$ be generalized?

$$RSH + N_2O_3 \rightarrow RSNO + HONO \quad (1)$$

- What is the subsequent RSNO reactivity with RSH?

$$RSNO + RSH \rightarrow RSSR + HNO \quad (2)$$
$$\rightarrow RSSH + RNO \quad (3)$$

This work: a study of the next thiol, R=CH_3

- Can the reaction $H_2S + N_2O_3 \rightarrow HSNO + HONO$ be generalized?

$$CH_3SH + N_2O_3 \rightarrow CH_3SNO + HONO \quad (1)$$

- What is the subsequent RSNO reactivity with RSH?

$$CH_3SNO + CH_3SH \rightarrow CH_3SSCH_3 + HNO \quad (2)$$
$$\rightarrow CH_3SSH + CH_3NO \quad (3)$$

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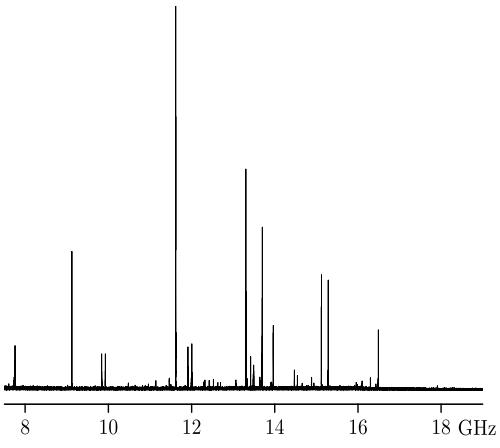
AMDOR spectroscopy + kinetic measurements

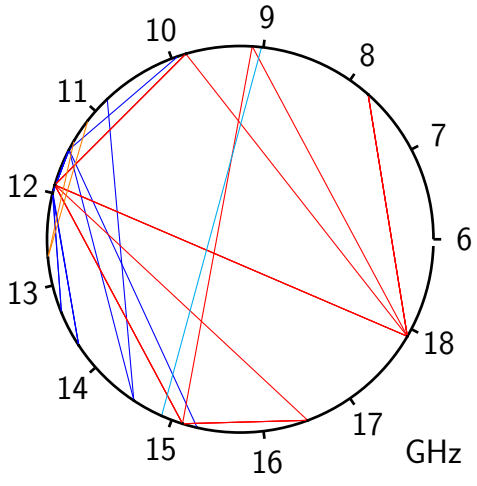
AMDOR spectroscopy of the $CH_3SH + NO$ mixture

1D spectrum



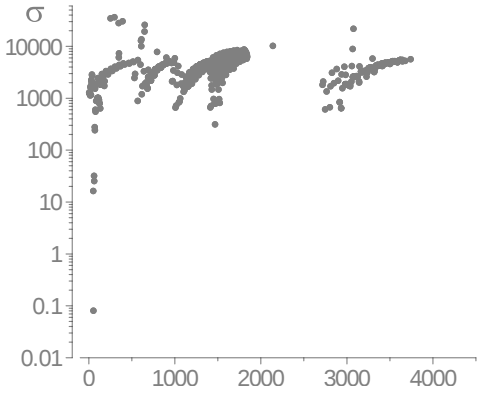
Identify unknown lines

2D spectrum



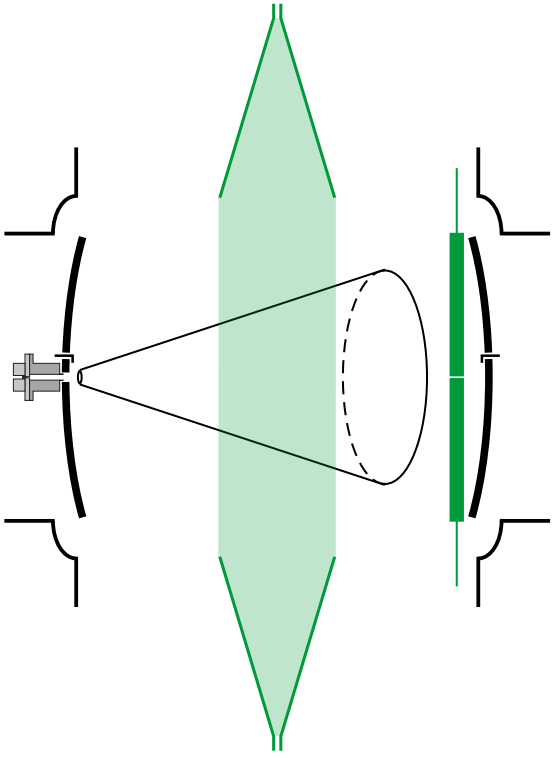
Establish linkages

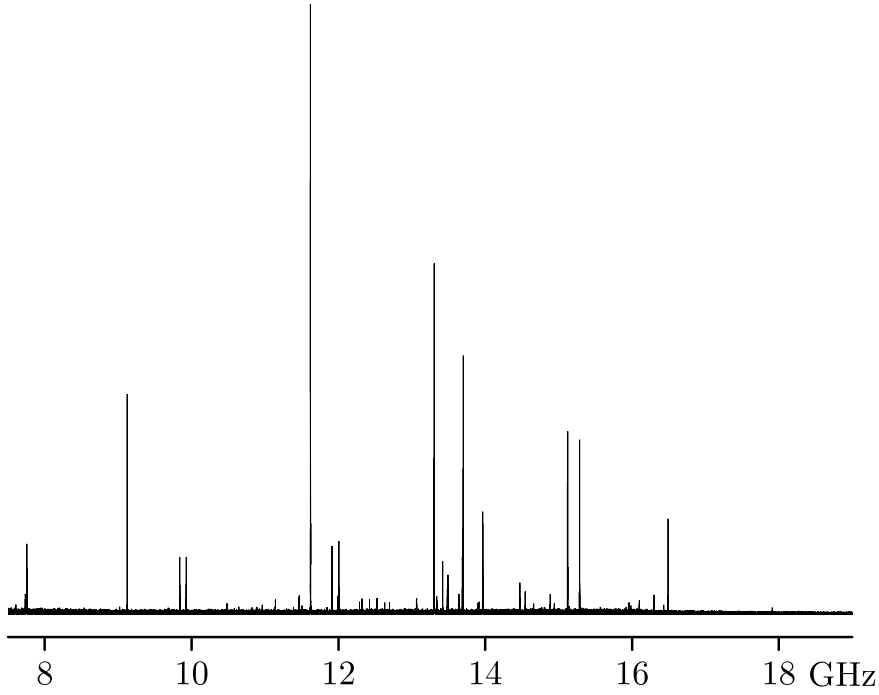
Analysis



Determine rotational constants

Step 1: Record CP spectrum



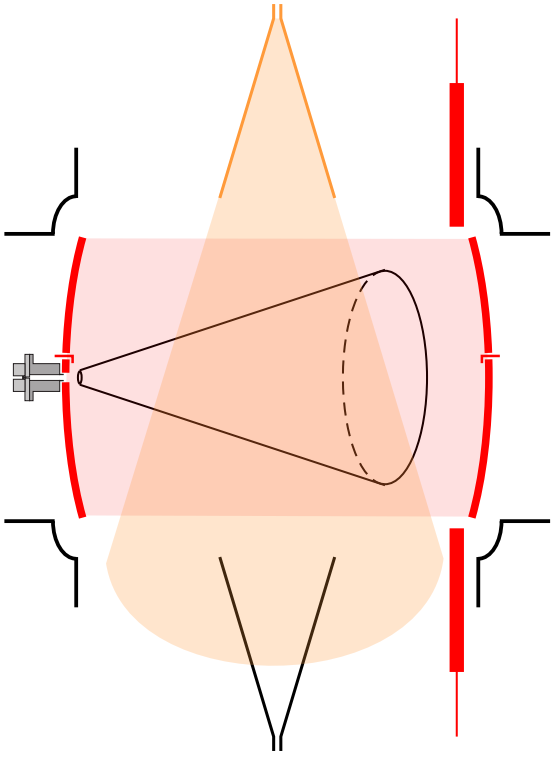


- CH_3SH + NO mixture
- 1000 shots ($\sim$ 3 min)
- Standard nozzle configuration

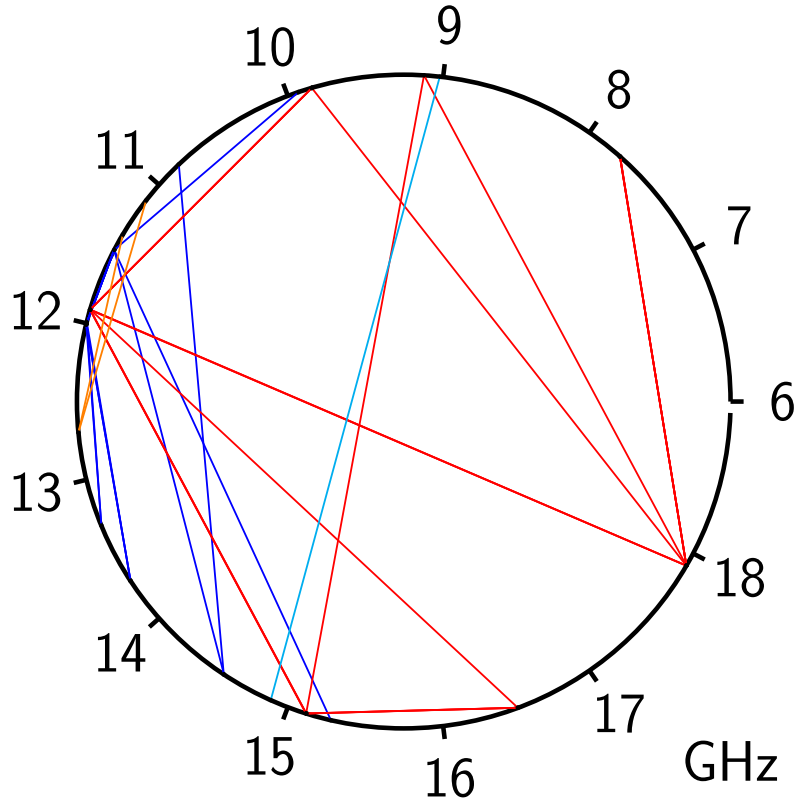
Known transitions:
CH_3SH, CH_3SSCH_3

$\sim$ 100 new lines

Step 2: Extensive DR tests

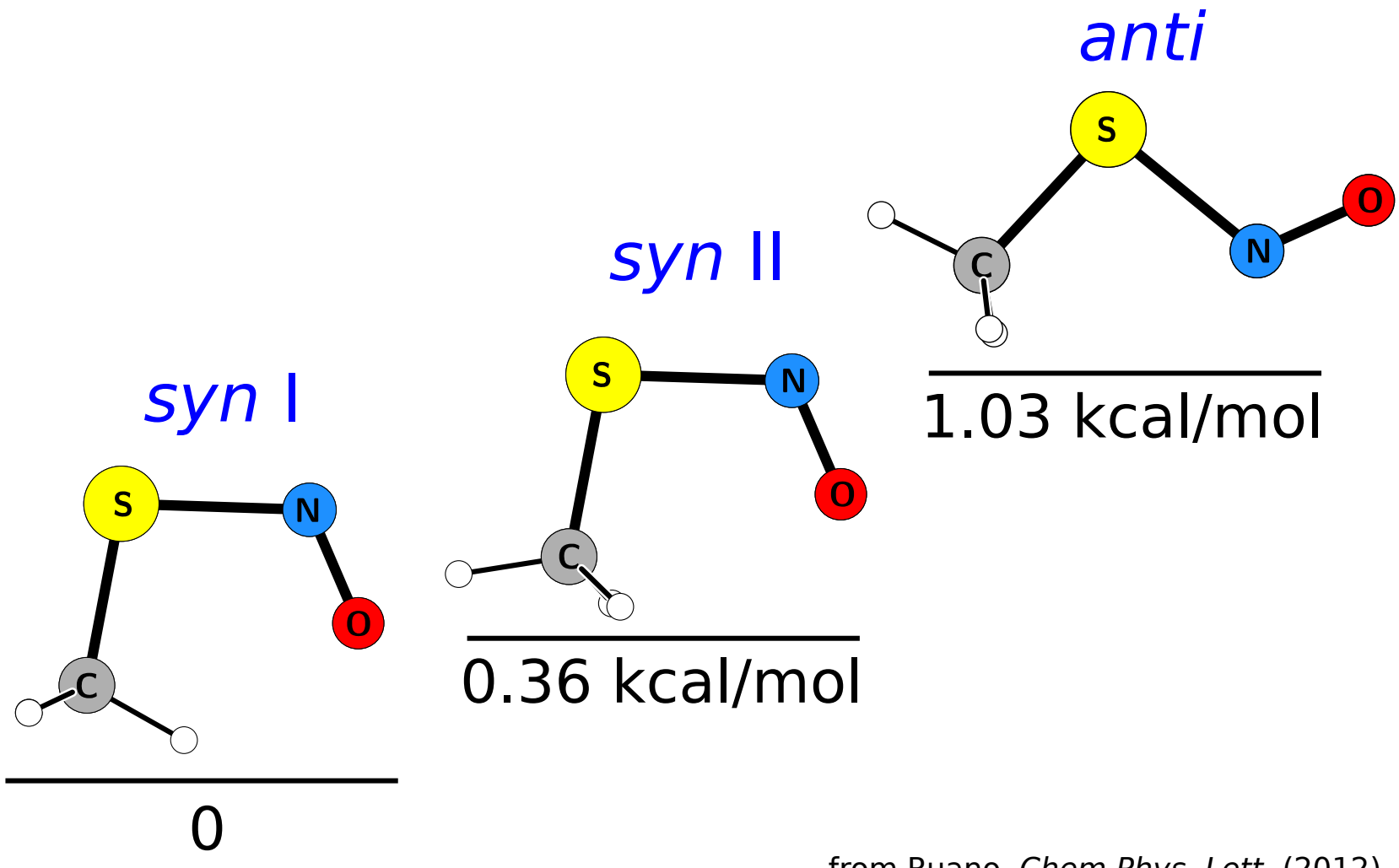


$\sim$ 8 h
38 DR matches



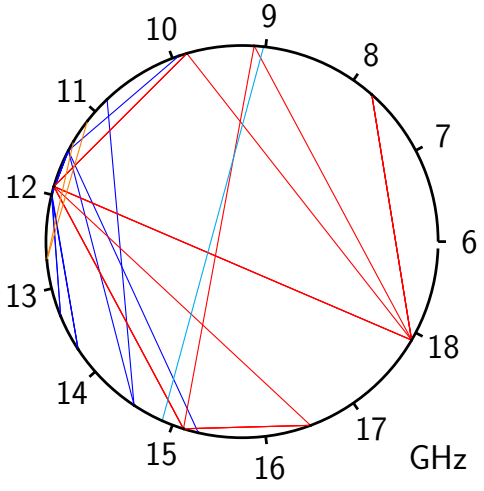
4 series, 2 distinct networks
not possible to use existing python scripts because CH_3SNO too light

CH_3SNO: 3 conformers predicted to be low-lying and stable



from Ruano, *Chem.Phys. Lett.* (2012)

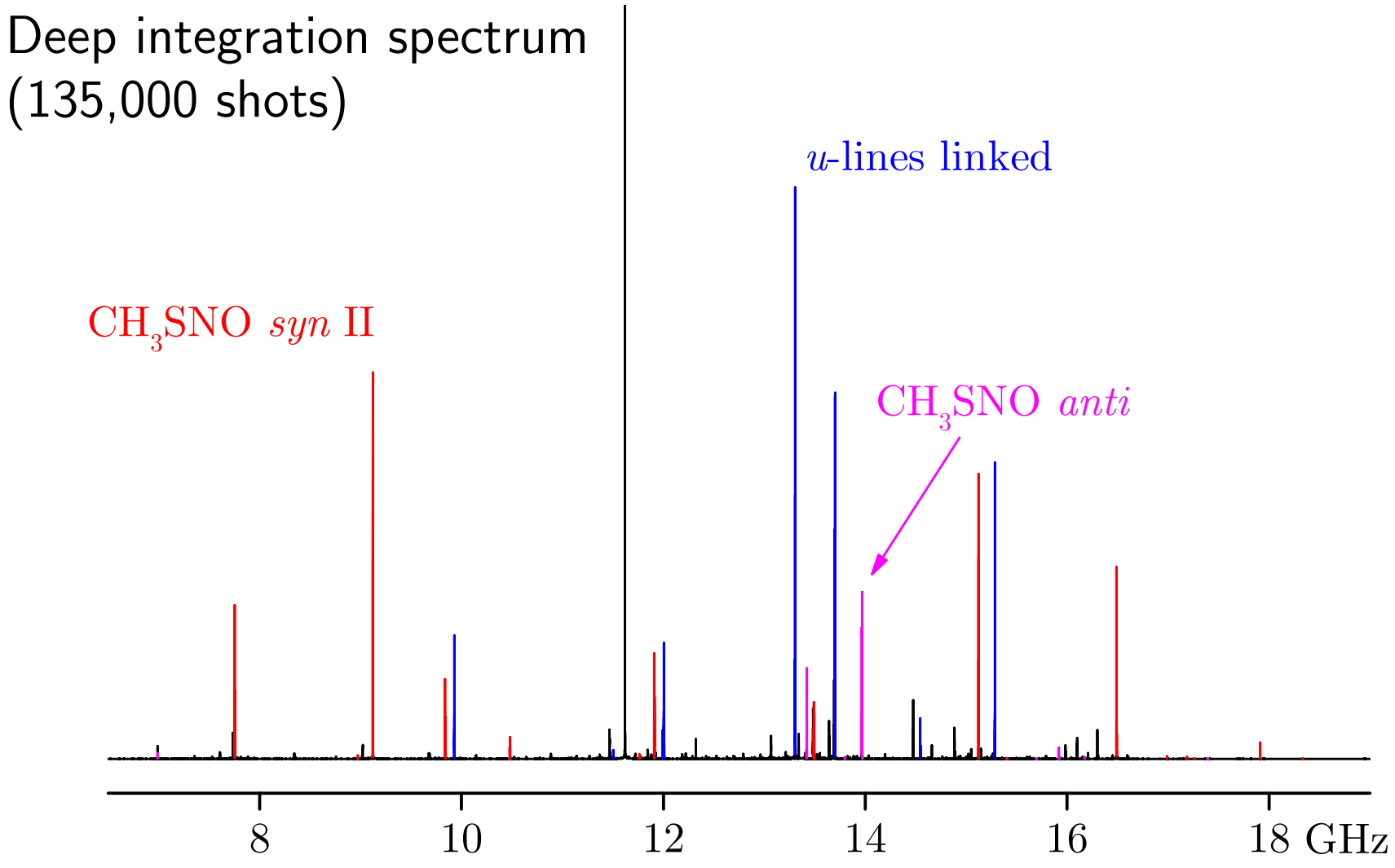
In combination with theory, two conformers of CH_3SNO identified



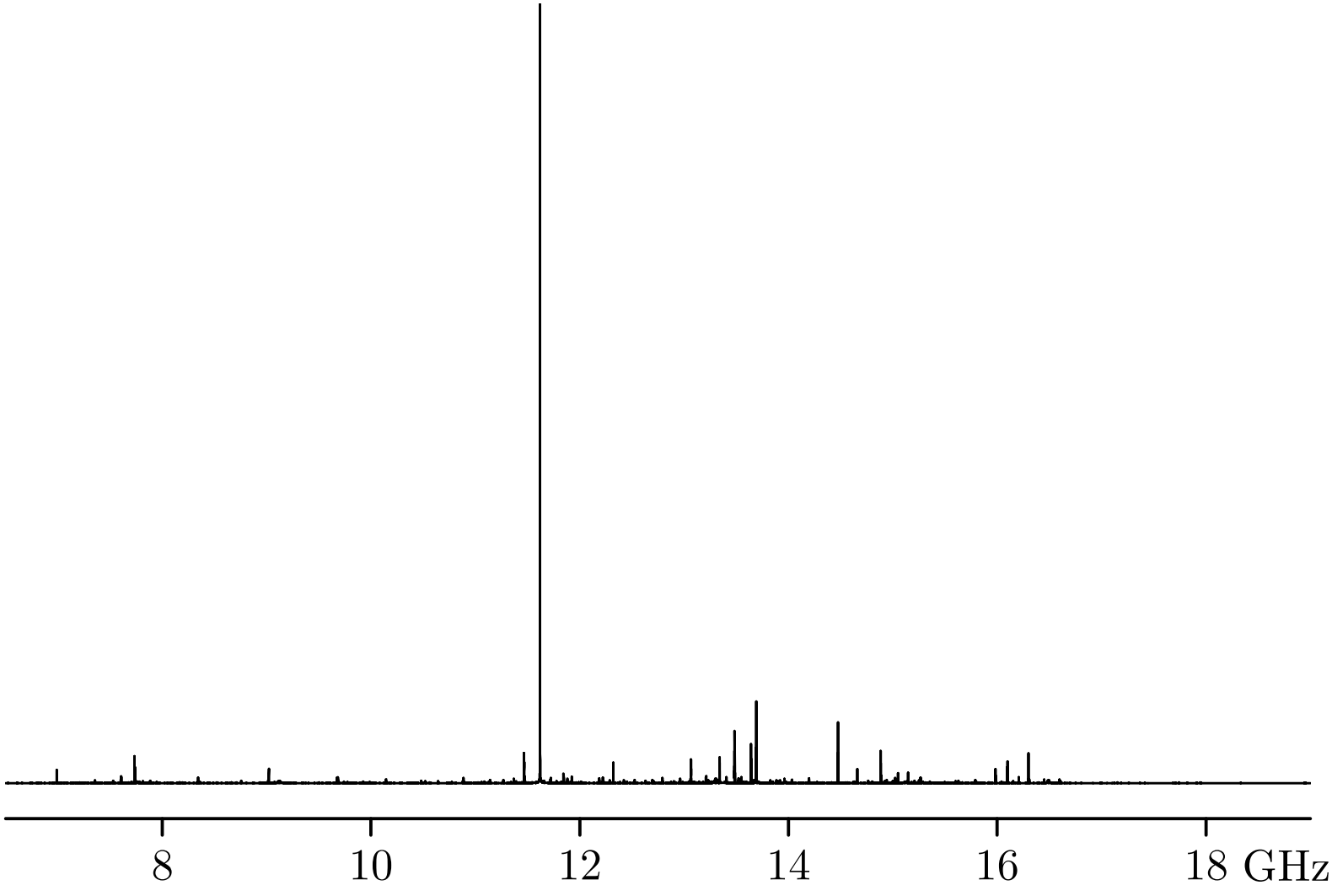
		Calc.[a]	**Exp.**	δ[b]
syn I	A_0	11 387.393		
	B_0	5129.127		
	C_0	3613.459		
syn II	A_0	11 291.812	11 438.301	1.013
	B_0	5382.575	5437.622	1.010
	C_0	3726.861	3683.954	0.988
anti[c]	A_0	19 177.202	19 133.110	0.998
	B_0	3783.713	3776.960	0.998
	C_0	3219.940	3214.384	0.998

[a] CCSD(T)/pwCVQZ
[b] Scaling factor
[c] Assigned on a deep integration spectrum

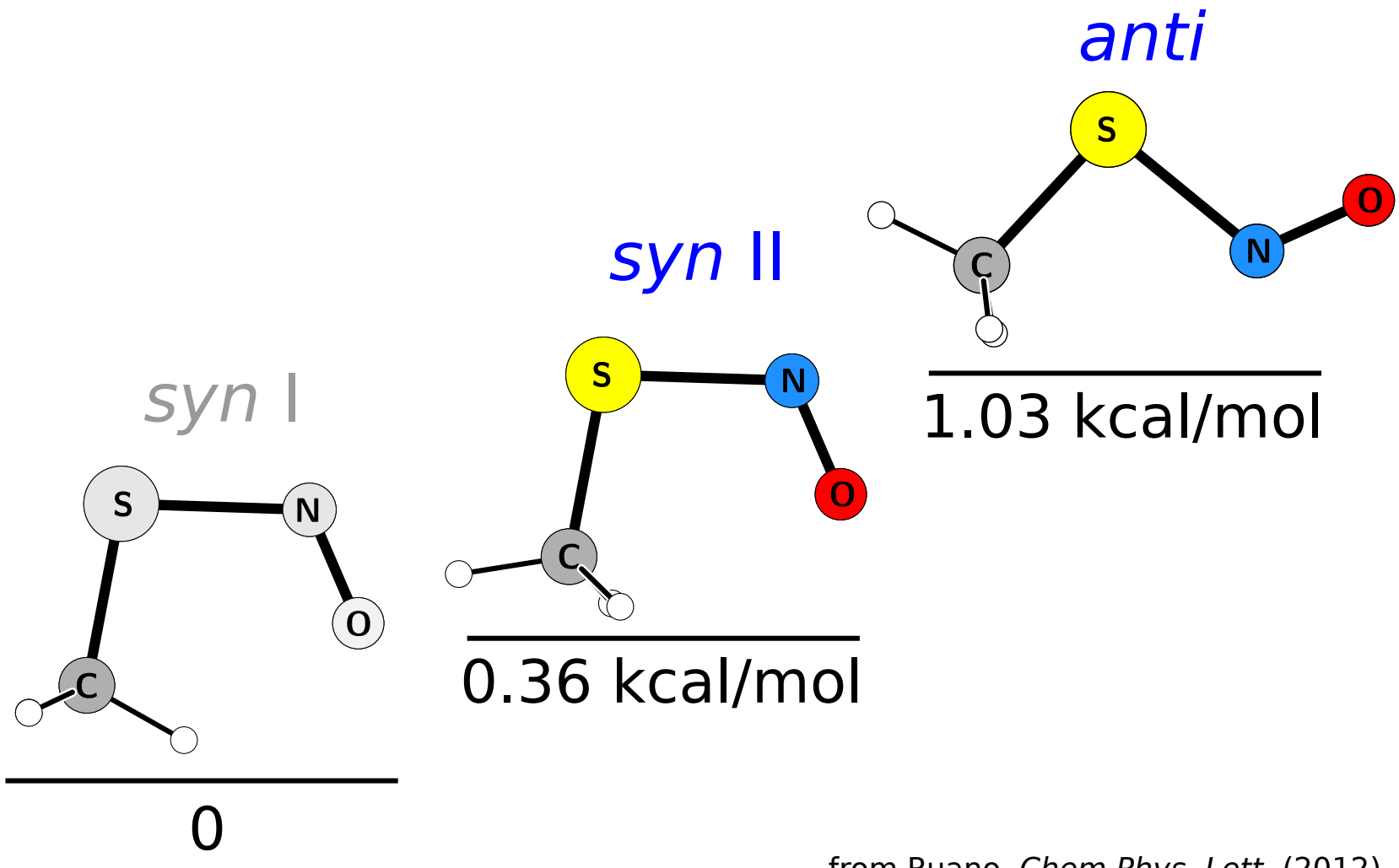
Some of the stronger lines remain unassigned



Additional DR measurements are needed to link remaining lines

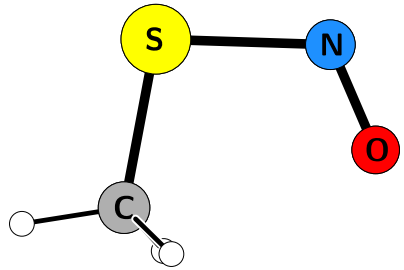


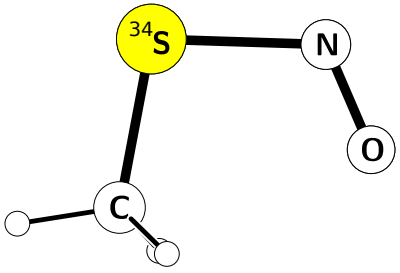
CH_3SNO: No definitive evidence for the *syn* I conformer



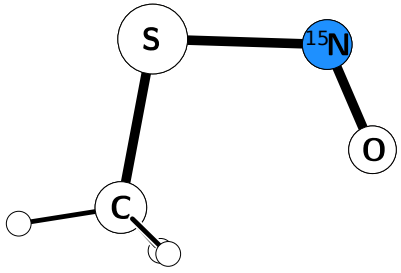
from Ruano, *Chem.Phys. Lett.* (2012)

Extensive isotopic spectroscopy for *syn* II

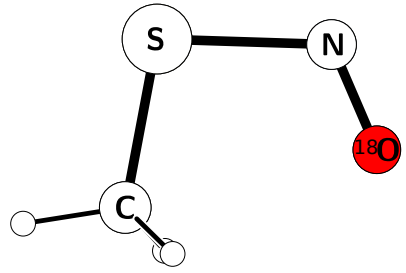




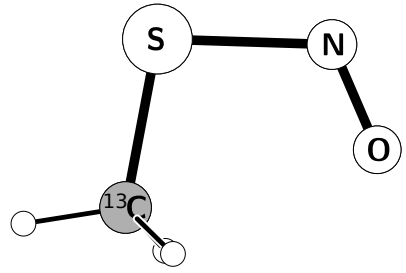
^{34}S in natural abundance (analyzed)



^{15}N from ^{15}NO (measured)

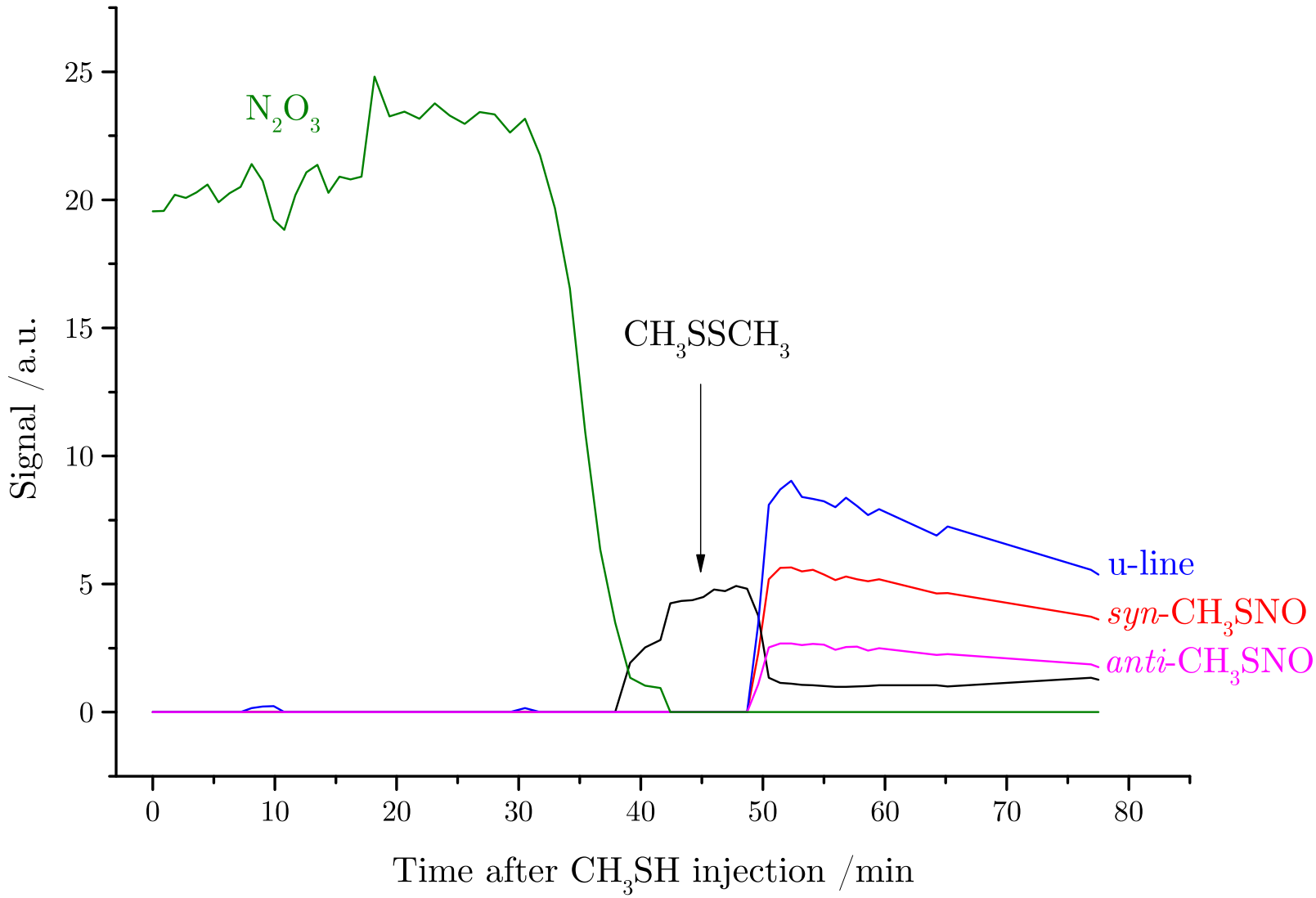


^{18}O from $H_2^{18}O$ (measured)



^{13}C in natural abundance (feasible in cavity)

Time evolution of reactants and products: Answers and new questions



An incomplete explanation of kinetic results

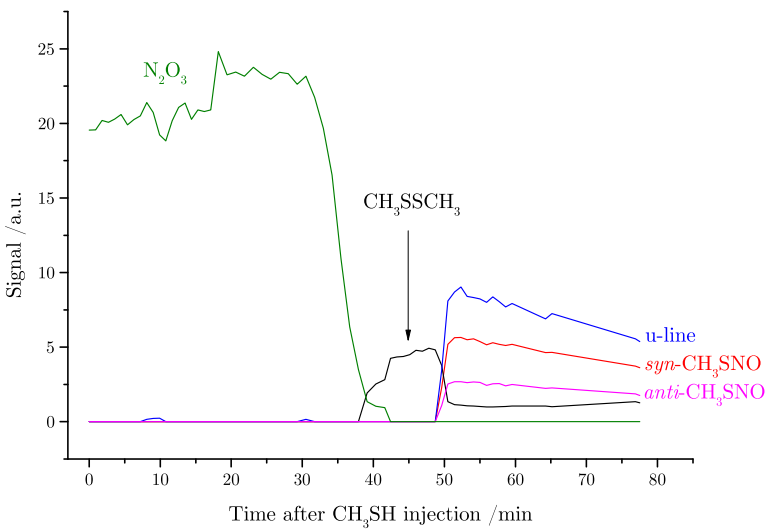
$$CH_3SH + N_2O_3 \rightarrow CH_3SNO + HONO \quad (1)$$

$$CH_3SNO + CH_3SH \rightarrow CH_3SSCH_3 + HNO \quad (2)$$

$$\rightarrow CH_3SSH + CH_3NO \quad (3)$$

- rate of Eq. (1) slow
- rate of Eq. (2) faster than (1)
- Eq. (3), no evidence on timescale of experiment

Open questions



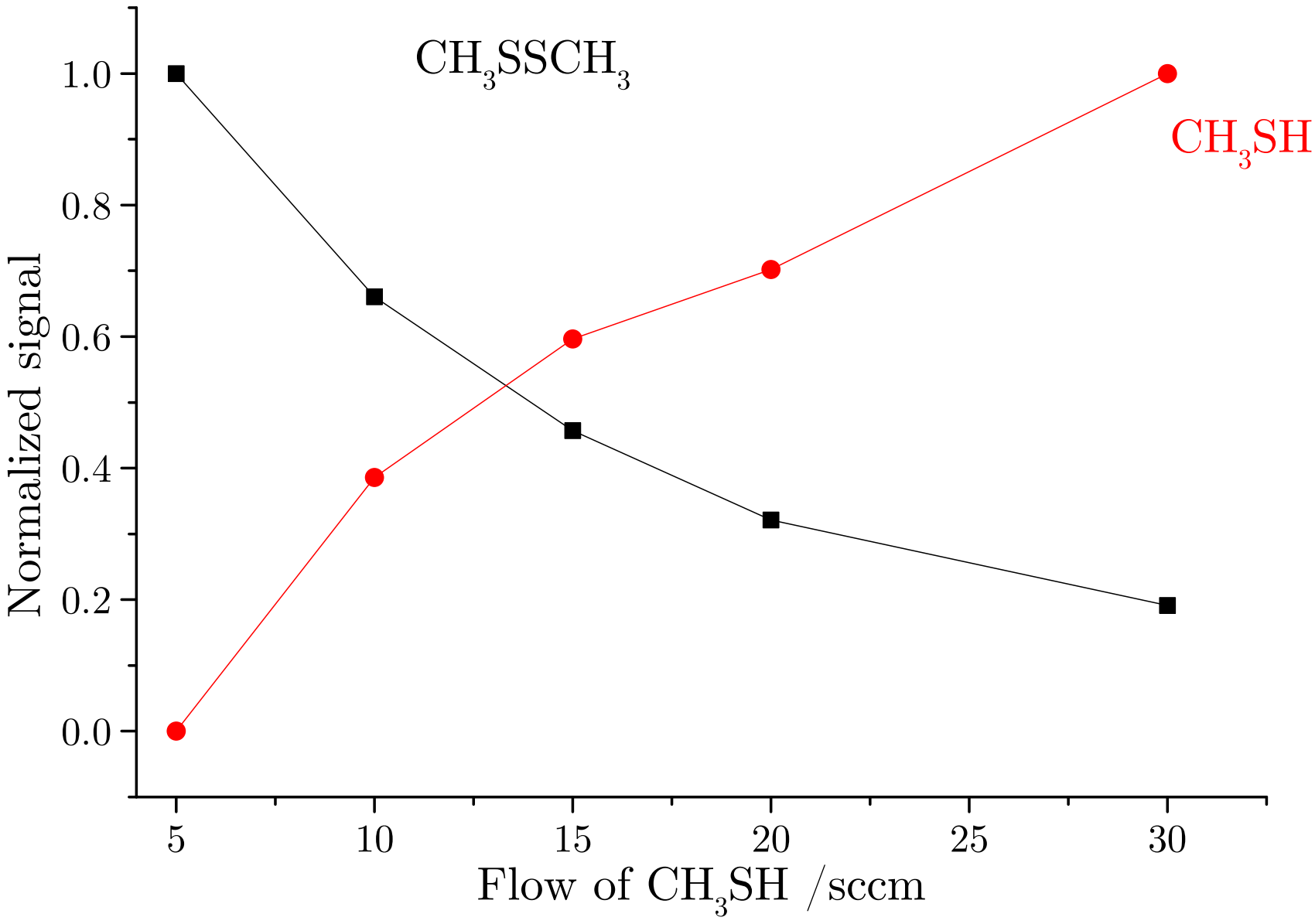
Identity of remaining u-lines?

- exhibit identical behavior as two CH_3SNO isomers

Is CH_3SSCH_3 a product or an intermediate of reaction?!

- observed before CH_3SNO
- signal decreases when CH_3SNO increases

CH_3SSCH_3 reactivity with CH_3SH



Summary & Conclusions

- AMDOR spectroscopy has enabled rapid identification of two CH_3SNO isomers

- Automatic assignment of spectral features can likely be made more efficient using targeted DR tests and more robust algorithms

New insight into CH_3SNO formation and reactivity:

- Like HSNO, CH_3SNO is readily formed, but appears more stable; other thiols might be studied by similar means

- Evidence for HNO remains elusive

Acknowledgements

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