Laboratory detection of 2,5- and 2,4-cyclohexadien-1-thione

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Abstract

- This study aims to detect sulfide aromatic molecules in space.
- The rotational transitions of 2,5- and 2,4-cyclohexadien-1-thione have been measured in the 8–26 GHz region in the laboratory.
- These molecules have been produced by supersonic jet discharge using a sample of thiophenol diluted by a buffer gas of Neon.
- The rotational constants have been determined.
- The measured frequencies can now be used for astronomical detection.

Introduction

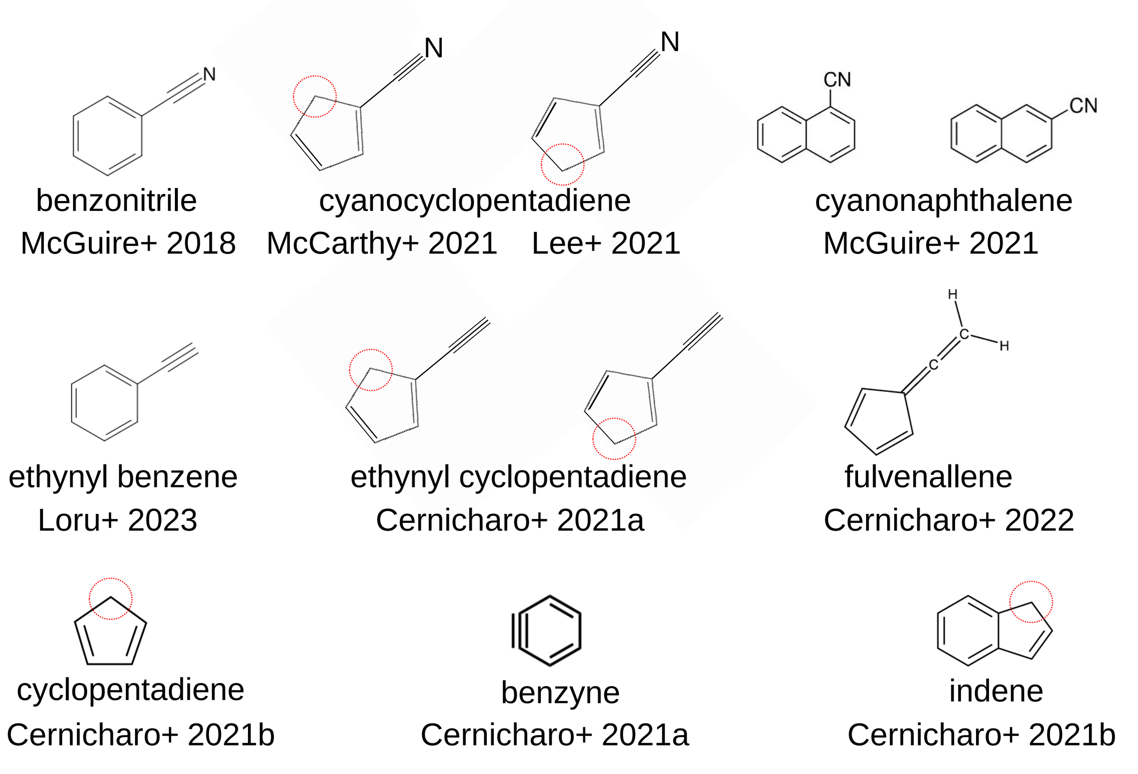

Figure 1 Observed sulfide aromatic molecules in space

- The 325 species of interstellar molecules have been found in space (Araki).
- The most recent appearance of a new molecular group has started since the discovery of benzonitrile by McGuire et al. (2018) in the Taurus molecular cloud 1 (TMC-1). At present 12 species have been detected except for benzene (Cernicharo et al. 2001) (Figure 1). Half of them have a doubly hydrogenated carbon (-CH_2-) in the ring (red circles in Figure 1).
- However, sulfide aromatic molecules have not been detected yet, although sulfide species accounts for 12% of the 325 species.
- Lack of rest frequency data of sulfide aromatic molecules by laboratory spectroscopy would be the main reason for the undiscovered.
- To find a sulfide aromatic molecule, a molecule having strong rotational lines need to be investigated.

- 2,5- and 2,4-cyclohexadien-1-thione do not have split by spin-rotation interaction, internal rotation, and hyperfine and have large dipole moments.
- The two molecules make strong rotational lines and are the easiest sulfide aromatic molecules to detect in space as a first finding.

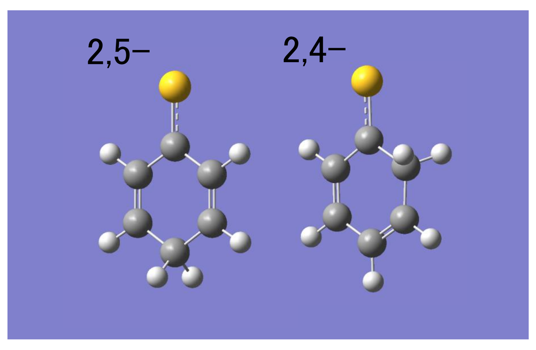

Figure 2
Molecular structures of 2,5- and 2,4-cyclohexadiene-1-thione

Experimental

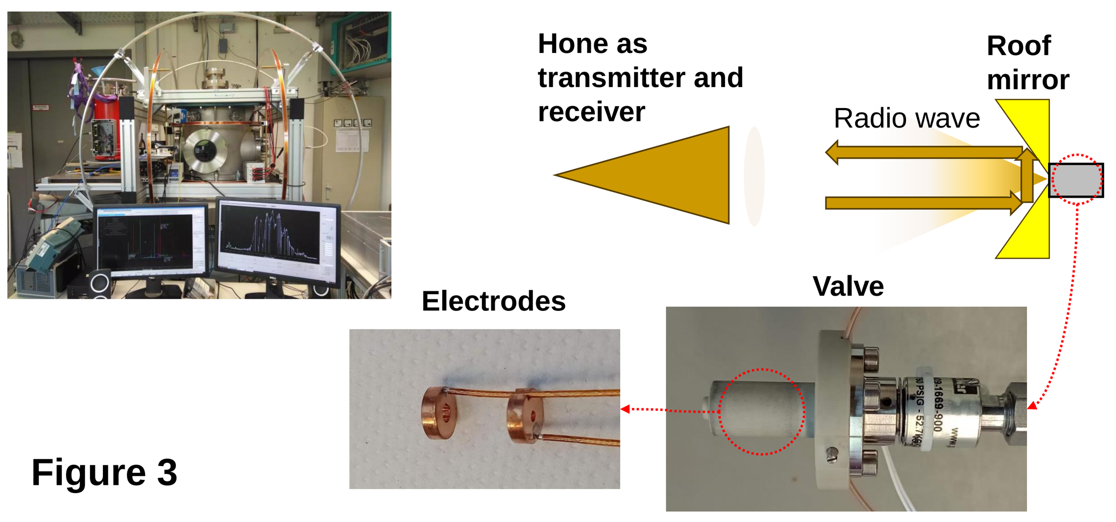

Figure 3

- Discharge: 10 Hz pulsed jet
- Temperature: 5 K
- Back pressure: 1.5 atom
- Voltage: 1000 V
- Current: 3–8 mA with a 50-kΩ ballast register
- Sample: thiophenol C_6H_5S in Ne, vapor pressure

- Lines were observed using the combination of the chirp pulsed spectrometer and the pulsed discharge supersonic jet.
- The wave source of this spectrometer consists of a synthesizer (Agilent Technologies, E8257D), an arbitrary waveform generator (Keysight, M8190A), and a solid-state amplifier (Microsemi).
- The output of the synthesizer after mixing with a chirped pulse from the arbitrary waveform generator was amplified by a solid-state amplifier and derived to a horn antenna.
- This horn antenna works as both an output port and a collecting port. Radio wave was received after interaction with gas.

Results and Discussion

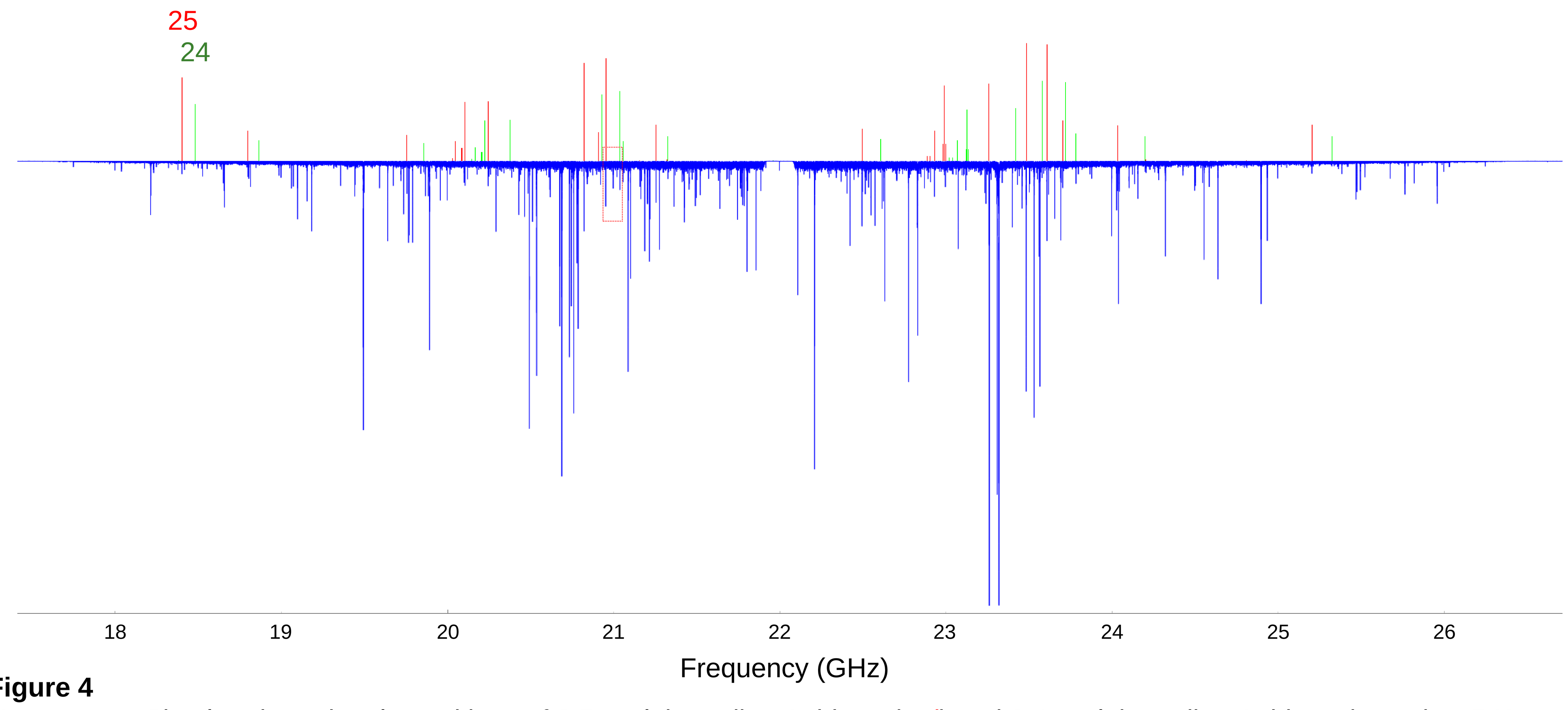

Figure 4
Upper trace: Simulated rotational transitions of 2,5-cyclohexadien-1-thione (red) and 2,4-cyclohexadien-1-thione (green) at 5 K
Lower trace: Observed rotational lines in the 18-26 GHz region. These lines include those of the sample gas, thiophenol, and the known discharge produces, CCCS, CCS, H_2CS, c-C_3H_2, and NH_3. The red dotted square area is expanded in Figure 5.

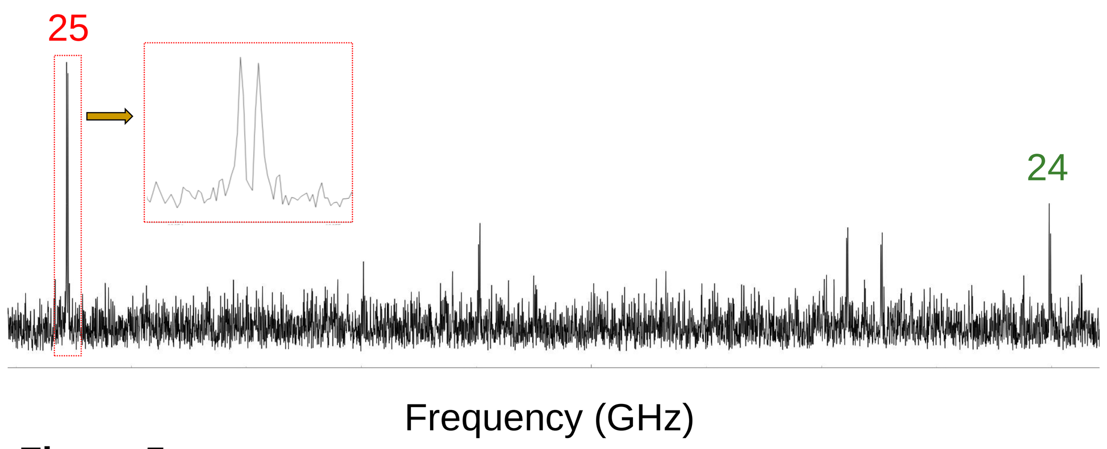

Figure 5
Expanded spectrum of the $J_{Ka,Kc}$ = $8_{1,8}$-$7_{1,7}$ transition for 2,5- and 2,4-cyclohexadien-1-thione
Double peaks in the red square is by Doppler splitting.

Table 1.
Measured Frequencies of Rotational Transitions for 2,5- and 2,4-cyclohexadien-1-thione in MHz

	2,5-cyclohexadien-1-thione		2,4-cyclohexadien-1-thione	
$N_{Ka,Kc}$'– $N_{Ka,Kc}$"	ν_{obs}	$\nu_{obs}-\nu_{calc}$	ν_{obs}	$\nu_{obs}-\nu_{calc}$
4 1 4 – 3 1 3				
4 0 4 – 3 0 3				
4 2 3 – 3 2 2				
4 2 2 – 3 2 1				
4 1 3 – 3 1 2				
5 1 5 – 4 1 4				
5 0 5 – 4 0 4				
5 2 4 – 4 2 3				
5 3 3 – 4 3 2				
5 3 2 – 4 3 1				
5 1 4 – 4 1 3				
6 1 6 – 5 1 5				
6 0 6 – 5 0 5				
6 2 5 – 5 2 4				
6 3 3 – 5 3 2				
7 1 7 – 6 1 6	*abbr.*		*abbr.*	
7 0 7 – 6 0 6				
7 2 6 – 6 2 5				
7 3 5 – 6 3 4				
7 3 4 – 6 3 3				
7 1 6 – 6 1 5				
7 2 5 – 6 2 4				
8 1 8 – 7 1 7				
8 0 8 – 7 0 7				
8 2 7 – 7 2 6				
8 3 6 – 7 3 5				
8 3 5 – 7 3 4				
9 1 9 – 8 1 8				
8 1 7 – 7 1 6				
9 0 9 – 8 0 8				
8 2 6 – 7 2 5				
9 2 8 – 8 2 7				
9 3 7 – 8 3 6				
10 1 10 – 9 1 9				

Table 2.
Molecular constants of 2,5- and 2,4-cyclohexadien-1-thione in MHz

	2,5-cyclohexadien-1-thione		2,4-cyclohexadien-1-thione	
	Obs. [a]	Calc. [b]	Obs. [a]	Calc. [b]
A_0		5356.0		5319.2
B_0	*abbr.*	1624.3	*abbr.*	1630.2
C_0		1255.6		1257.1
Δ_J	0.0[c]	0.000054	0.0[c]	0.000058
Δ_K	0.0[c]	0.001002	0.0[c]	0.000928
$\Delta_{J,K}$	0.0[c]	0.000225	0.0[c]	0.000245
δ_J	0.0[c]	-.000014	0.0[c]	0.000015
δ_K	0.0[c]	-.000252	0.0[c]	0.000178
RMS[d]	0.017		0.031	

[a] Values in parentheses denote the uncertainties (1σ) and apply to the last digit of the values.
[b] CAM-B3LYP/cc-pVTZ using Gaussian 16W
[c] Fixed
[d] spfit

Examples of frequency estimation in a millimeter region
$J_{Ka,Kc}$ = $17_{0,17}$-$16_{0,16}$
2,5- 43474.442±0.460 MHz
2,4- 43638.774±0.112 MHz

Table 3.
The dipole moments of 2,5- and 2,4-cyclohexadien-1-thione by CAM-B3LYP/cc-pVTZ using Gaussian 16W

	2,5-	2,4-
μ_a (D)	4.73	3.88
μ_b (D)		0.52
Relative Energy (K)	0	1780

Summary

- The 34 and 18 rotational transitions of 2,5- and 2,4-cyclohexadien-1-thione in the centimeter wave region have been measured in the laboratory.
- Molecular constraints of both the molecules have been determined.
- Rest frequencies of the molecules have been expected accurately in a millimeter region (< 1 MHz except for the higher *K* transitions).

References

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Future plan

- The millimeter region needs to be searched in the laboratory.
- We plan to investigate these molecules in an astronomical database.

List of the observed interstellar molecules

http://molecules-in.space/