Microwave Spectroscopy and Formation Chemistry of HCCSH

Investigation of Thioketene isomers

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Carbon-sulfur molecules

Unique chemical properties of carbon-sulfur bonds

- Biomolecules
- Astronomical molecules
- Chemical synthesis
Carbon-sulfur chains are prominent in the interstellar medium

- $C_nS$ has been detected in cold molecular clouds (TMC-1)
- Extensive laboratory and astronomical work
Thioketene

One of the simplest carbon-sulfur molecules

- Isoelectronic with ketene

- Rapidly polymerize in condensed phase

- Extended derivatives of thioketene are less reactive
Thioketene Isomers

![Relative energy (kJ/mol) for different thioketene isomers: H₂CCS, HCCSH, c-H₂C₂S.]
Ethythiol

Second lowest energy isomer of \( \text{H}_2\text{C}_2\text{S} \) family

Early work by Krantz and Laureni using matrix isolation

Detection with IR, photolysis of thiadazole

Formation pathway unclear

The possibility that products arise from recombination of photochemically generated sulfur atoms with acetylene can be explored in two ways (eq 5).

\[
\begin{align*}
\text{S} & \xrightarrow{\text{hv} ?} \text{HC} & \text{CH} \\
& + \text{S} & \xrightarrow{\text{P}} \text{H}_2\text{C} & \text{C} & \text{S} \\
& & \text{HC} & \text{C} & \text{SH}
\end{align*}
\]

Tools of the Trade
Cavity-enhanced Fourier Transform Microwave Spectrometer

5 - 43 GHz
Excitation Pulse

RF Synthesizer

Excitation Pulse

RF Receiver
Doppler splitting
Recipe for HCCSH

Electrical discharge of:

- HCCCH
- H₂S

Shaken, not stirred
Coupled-Cluster calculations using electronic structure package, CFOUR

- Geometry optimizations of HCCSH performed at the CCSD(T)/cc-pCVXZ level
- Equilibrium rotational constants
- Dipole moments and centrifugal distortion terms
Microwave spectroscopy of HCCSH
$\mu_a = 0.1 \text{ D}$
$\mu_a = 0.1 \text{ D}$

$\mu_b = 0.8 \text{ D}$
First approximation of $\alpha$-type spectrum

$$\nu_{\alpha} \approx (J'' + 1)(B + C)$$
First approximation of $a$-type spectrum

$$\nu_a \approx (J'' + 1)(B + C)$$

Predicted fundamental:

$\sim 10988$ MHz
$\alpha$-Type Rotational Spectrum

First approximation of $\alpha$-type spectrum

Predicted fundamental:

$\nu_{\alpha} \approx (J'' + 1)(B + C)$

~10988 MHz
$\alpha$-Type Rotational Spectrum

First approximation of $\alpha$-type spectrum

Predicted fundamental:
$\sim 10988$ MHz

Measured fundamental:
$10985.9808$ MHz

O-c:
$\sim 2$ MHz ($0.02\%$)
Identifying the carrier

Requires discharge

Closed-shell electronic configuration

Frequencies fit to effective linear molecule Hamiltonian
Isotopic Spectroscopy

Measure the same transitions for the different isotopologues

- Frequency shifts should be consistent with change in mass
- Natural abundance and isotopic substitution
Isotopic Spectroscopy

\[ \text{SH} + \text{C}_2\text{H} \rightarrow \text{HSCCH} \]

\[ \text{D}_2\text{S} \quad \downarrow \quad \text{DCCCD} \quad \downarrow \quad \text{H}^{13}\text{CCH} \quad \downarrow \quad \text{H}^{13}\text{C}^{13}\text{CH} \]

\[ \text{DSCCH} \quad \quad \downarrow \quad \text{HSCCD} \quad \downarrow \quad \text{HS}^{13}\text{CCH} \quad \downarrow \quad \text{HS}^{13}\text{C}^{13}\text{CH} \]

\textit{ab initio} constants can be empirically scaled to predict isotopic data
Natural Abundance

4.25%

$\text{D}_2\text{S} + \text{HCCCH}$

$\text{H}_2\text{S} + \text{DCCCD}$

$\text{H}^{34}\text{SCCH}$

$\text{DSCCH}$

$\text{HSCCD}$
HCCCH
H$^{13}$CCH
HC$^{13}$CH
H$^{13}$C$^{13}$CH

Statistical $^{13}$C Mixture

Offset Frequency (MHz)

HCCH + H$^{13}$C$^{13}$CH mixture

Offset Frequency (MHz)
Formation Mechanism

Isotopic substitution indicates:

- $C_2H$ unit remains intact
- $SH$ unit remains intact

Inferred recombination of $SH + C_2H$

Involves electronically excited reactants?

$SH \ A \ ^2\Sigma$

$C_2H \ A \ ^2\Pi$

$C_2H \ X \ ^2\Sigma$

$SH \ X \ ^2\Pi$

$HCCSH \ X \ ^1\ A''$
Two Spectra, One Molecule

Non-zero dipole moments along both \( a \) and \( b \) axes

- \( b \)-type spectrum not accessible directly in FT

- Bootstrap to high frequencies using double resonance

- \textit{ab initio} constants predict fundamental \( b \) type transition at \(~296 \text{ GHz}\)

\[
\mu_a = 0.1 \text{ D} \\
\mu_b = 0.8 \text{ D}
\]
Double Resonance Measurements

Additional 5 $b$-type transitions allowed $A$
constant to be determined

- Measurements extended properly into mm-wave by absorption experiments at CNRS

- Preliminary DR constants guided mm-wave measurements
HCCSH Global Fit

Combined fit with FT-cavity and millimeter-wave absorption lines

- Total of 100 lines measured
- Average fit RMS of 43 kHz
Obligatory Table of Constants (MHz)

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>291414.3373(235)</td>
</tr>
<tr>
<td>B</td>
<td>5547.68737(58)</td>
</tr>
<tr>
<td>C</td>
<td>5438.29875(74)</td>
</tr>
<tr>
<td>$D_J$</td>
<td>$1.3988(82) \times 10^{-3}$</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>0.13627(32)</td>
</tr>
<tr>
<td>$D_K$</td>
<td>19.8358</td>
</tr>
<tr>
<td>$d_J$</td>
<td>$0.029253(48) \times 10^{-3}$</td>
</tr>
<tr>
<td>$d_K$</td>
<td>0.0734121</td>
</tr>
<tr>
<td>$\Phi_J$</td>
<td>$3.15(229) \times 10^{-9}$</td>
</tr>
<tr>
<td>$\phi_J$</td>
<td>$3.68(77) \times 10^{-11}$</td>
</tr>
</tbody>
</table>
Conclusions

Identified two new molecules by spectroscopic signatures and isotopic substitution with FT-microwave

- 28 lines, 7 isotopologues

- Extended mmw measurements on main isotopologue

- Reaction pathway involves radical recombination
Future Work

- Astronomical search with SOFIA in the THz region
- Extend inventory to new species of isomer family
- Comparison of abundances may reveal oxygen/sulfur dynamics in ISM
Thank You!