

## Microwave Spectra of Thioketene and Four of Its Isotopic Species

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Milligram quantities of thioketene,  $S=C=CH_2$ ,  $S=^{13}C=CH_2$ ,  $S=C=^{13}CH_2$  and  $S=C=CH^2H$  (or  $S=C=CHD$ ) have been produced by pyrolysis at 1100 K of thiadiazol,  $\underline{S}-N=N-CH=CH$ ,  $\underline{S}-N=N-CH=^{13}CH$ ,  $\underline{S}-N=N-^{13}CH=CH$  and  $\underline{S}-N=N-CH=C^2H$  at a pressure of 10–15 mTorr. Microwave spectra (18.6–40.0 GHz) of the isotopic group of thioketenes were recorded,  $^{34}S=C=CH_2$  being studied in natural abundance. Rotational constants  $B$  and  $C$  were obtained for five species in their ground states. All  $R$ -type and practically all  $Q$ -type  $\mu_a$ -transitions between 18.6 and 40.0 GHz were assigned. During the pyrolysis scrambling of C(4) and C(5) in thiadiazol and migration of H(5) definitely occur. Although the 3-membered ring compound thiirene,  $\underline{CH=CH-S}$ , ethynyl mercaptan,  $H\equiv C-SH$  and  $N\equiv N-S$ , were sought after, they were not observed.

Thioketene (I, Fig. 1) was first obtained by pyrolysis of  $(CH_3)_3C-S-C\equiv CH$  and tentatively identified by its IR-spectrum.<sup>1</sup> Later, Kroto and collaborators

found I among the products of pyrolysis of trithioacetone,  $(CH_3CSCH_3)_3$ , by recording its  $R$ -type low- $J$  ( $\leq 4$ )  $\mu_a$ -transitions between 26.5 and 40.0 GHz. They reported a structure of I based on further microwave spectra of naturally occurring II (1%), III (1%), V (4%) and enriched samples of IV and of 3,3'- $H$ -thioketene.<sup>2,3</sup> Experimental frequencies on I were published.<sup>2</sup> Prior to their final paper<sup>4</sup> the present authors were studying the pyrolysis of thiadiazol (VI, Fig. 2) and isotopically marked species VII–IX<sup>5</sup> as a contribution to a current discussion on the existence of 3-membered rings (here thiirene, Fig. 3) as intermediates of final products of photolysis and/or pyrolysis of 5-membered rings.<sup>6–8</sup> Under these circumstances *all* sufficiently intense microwave transitions assignable to I–V in the investigated region (18.6–40.0 GHz) had to be identified under a simultaneous search for species such as thiirene (XI),  $HC\equiv C-SH$  (XII),  $N_2S$  (XIII), *etc.*

The transitions reported in Ref. 4 suffice for a determination of the structure of I in its ground

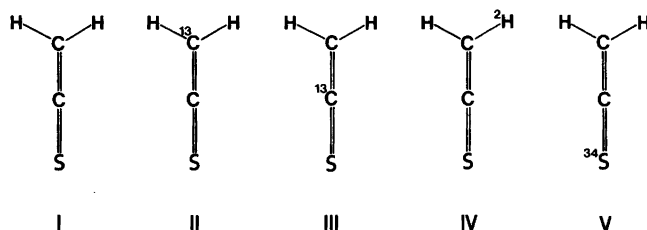


Fig. 1. Thioketene (I) and monosubstituted isotopic thioketenes (II–V). Samples of II–IV were *ca.* 95% enriched. V was studied in natural abundance (4%).

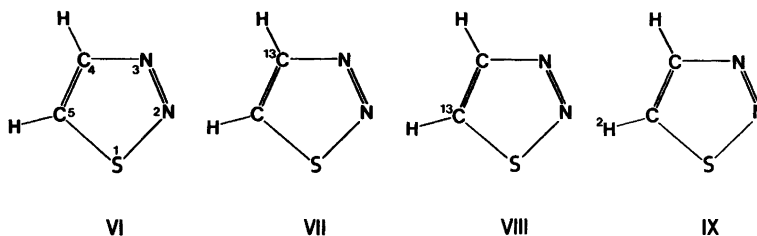


Fig. 2. Thiadiazole (VI) and isotopically labelled thiadiazoles (VII–IX).  $^{34}\text{S}$ -Thiadiazole denoted by X in text.

state. The data were kindly communicated to us before publication.<sup>4</sup> Some of the data given here (Table 1) are frequencies of  $Q$ -type, high- $J$  ( $\leq 26$ )  $\mu_a$ -transitions of little, if any, significance to the ground state structure of I, as reported in Ref. 4. They provide, however, a close analysis of the distortion constants of I so that, for example, transition frequencies in astrophysically accessible regions at 70 GHz and higher can be predicted with improved precision.

## EXPERIMENTAL

Pyrolysis of VI and microwave analysis of polar products were performed as described earlier.<sup>9</sup> In the present case vapors of VI–IX were pumped through a hot (1100 K) quartz tube at a pressure of 10–15 mTorr directly into a conventional Stark spectrometer operating in the 18.6–40.0 GHz region ('K' and 'R' bands).

VI was prepared according to Ref. 10. The preparation of VII–IX will be described in a forthcoming paper. Microwave spectra of VI–IX have been analyzed by Stiefvater.<sup>11</sup> The intensity of the microwave absorption of VI at 33 487.70 MHz was used by us as a measure of the presence of 100% VI. The search for this transition under comparable conditions in our samples of VII–IX gives only dubious responses which lead us to conclude that their isotopic enrichment is 95% or higher. Also, sample VII was not "contaminated"

with VIII and *vice versa* (of importance for a later argument). Likewise, sample IX did not contain  $4\text{-}^2\text{H}$ -thiadiazol (spectrum in Ref. 11).

## RESULTS

All hitherto assigned rotational transitions of groundstate I–V (including the observations of Ref. 4) are collected in Table 1. The agreement between independent measurements in two laboratories is satisfactory.

Corresponding rotational and distortion constants are reported in Tables 2 and 3 as functions of assumed inertial defects,  $\Delta = I_c - I_b - I_a$  of 0.20, 0.00 and  $-0.20 \text{ u}\text{\AA}^2$ , in each case taken as equal for all five species. As seen from Table 3,  $T_4$  is well-defined while  $T_1$  and the assumed inertial defects are strongly correlated. Subsequently,  $I_a$  is known only within *ca.* 10%.

The complete microwave spectrum (recorded at different modulating voltages) involves lines assignable to vibrational satellites.<sup>4</sup> Aside from these, only a few unidentified weak lines occur. The main polar product formed by pyrolysis at 1100 K *etc.*, of VI is, therefore, thioketene.

For the sake of completeness the "chemical" results are given briefly. Our experiments show that  $\text{VI} \xrightarrow[1100 \text{ K}]{\text{I}}$  I while products XI, XII and XIII, (Fig. 3) were not observed. They may, however,

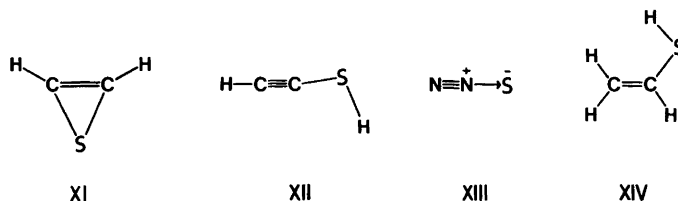


Fig. 3. Structural formulae of thiirene, ethynyl mercaptan, dinitrogen sulfide and ethenyl mercaptan (syn).

Table 1. Ground state rotational transition frequencies (MHz) for 5 isotopic species of thioketene.

Transition	$\text{H}_2^{12}\text{C}=\text{C}=\text{S}^{32}\text{S}$		$\text{H}_2^{13}\text{C}=\text{C}=\text{S}^{32}\text{S}$		$\text{H}_2^{12}\text{C}=\text{C}=\text{S}^{34}\text{S}$		$\text{H}^{2}\text{H}^{12}\text{C}=\text{C}=\text{S}^{32}\text{S}$	
	Obs.	Obs. - Calc. <sup>b</sup>	Obs.	Obs. - Calc. <sup>b</sup>	Obs.	Obs. - Calc. <sup>b</sup>	Obs.	Obs. - Calc. <sup>b</sup>
$1_{01} \rightarrow 2_{02}$	22407.92	0.03	21612.93	0.02	22341.92	0.03	21906.47	0.00
$1_{11} \rightarrow 2_{12}$	22292.31	0.03	21505.39	0.03	22227.00	0.03	21795.98	0.04
$1_{10} \rightarrow 2_{11}$	22522.24	0.05	21719.26	0.03	22455.55	0.03	22015.74	0.05
$2_{02} \rightarrow 3_{03}$	33611.71 <sup>a</sup>	-0.05	32419.27 <sup>a</sup>	-0.03	33512.72 <sup>a</sup>	-0.05	32859.58 <sup>a</sup>	-0.05
$2_{12} \rightarrow 3_{13}$	33438.43 <sup>a</sup>	0.01	32258.07 <sup>a</sup>	0.02	33340.46 <sup>a</sup>	0.00	32693.91 <sup>a</sup>	-0.00
$2_{11} \rightarrow 3_{12}$	33783.22 <sup>a</sup>	-0.06	32578.78 <sup>a</sup>	-0.06	33683.23 <sup>a</sup>	-0.04	33023.52 <sup>a</sup>	-0.02
$2_{21} \rightarrow 3_{22}$	33607.84 <sup>a</sup>	0.10	32415.63	0.09	33508.87 <sup>a</sup>	0.10	32855.75 <sup>a</sup>	0.09
$2_{20} \rightarrow 3_{21}$	33607.84 <sup>a</sup>	-0.08	32415.63	-0.07	33508.87 <sup>a</sup>	-0.09	32855.75 <sup>a</sup>	-0.08
$16_{1,16} \rightarrow 16_{1,15}$								
$18_{1,18} \rightarrow 18_{1,17}$	19652.36	0.10			19535.9	0.03	18784.0	0.13
$19_{1,19} \rightarrow 19_{1,18}$	21835.12	0.05	20311.96	0.11	21705.8	0.03	20870.2	-0.05
$20_{1,20} \rightarrow 20_{1,19}$	24132.57	-0.00	22449.20	0.05	23989.7	0.03	23066.2	-0.07
$21_{1,21} \rightarrow 21_{1,20}$	26544.68	-0.05	24693.09	-0.02			25372.0	0.11
$22_{1,22} \rightarrow 22_{1,21}$	29071.41	-0.08	27043.66	-0.05	28899.25	-0.11	27787.0	-0.05
$23_{1,23} \rightarrow 23_{1,22}$	31712.76	-0.05	29500.85	-0.05	31525.05	-0.01	30311.7	-0.02
$24_{1,24} \rightarrow 24_{1,23}$	34468.62	-0.01	32064.58	-0.06	34264.60	0.00		
$25_{1,25} \rightarrow 25_{1,24}$	37338.98	0.07	34734.86	-0.02	37117.93	0.03	35689.3	-0.11
$26_{1,26} \rightarrow 26_{1,25}$			37511.65	0.08			38542.4	0.09
r.m.s. <sup>b</sup>	0.072		0.069		0.063		0.084	
							0.122	

<sup>a</sup> Consistent with Kroto's measurements except where marked <sup>a</sup> (~0.2 MHz). <sup>b</sup> Obs. - Calc. and r.m.s. values (in MHz) for assumed inertial defect = 0.00. Rotational and distortion constants from Tables 2 and 3.

Table 2. Rotational constants  $B$  and  $C$  (MHz) of isotopic thioketenes for assumed  $-0.20 \leq \Delta \leq 0.20$  ( $\text{u}\text{\AA}^2$ ) as calculated by ROTFIT. Independent of  $\Delta$  within the indicated limits of error.  $\Delta = I_c - I_b - I_a$ .

Molecule	$B$	$C$
$\text{H}_2^{12}\text{C}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	$5659.4560 \pm 0.0073$	$5544.5000 \pm 0.0071$
$\text{H}_2^{13}\text{C}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	$5456.6996 \pm 0.0070$	$5349.7653 \pm 0.0068$
$\text{H}_2^{12}\text{C}=\text{}^{13}\text{C}=\text{}^{32}\text{S}$	$5642.6160 \pm 0.0065$	$5528.3412 \pm 0.0063$
$\text{H}_2^{12}\text{C}=\text{}^{32}\text{C}=\text{}^{34}\text{S}$	$5531.5592 \pm 0.0086$	$5421.6836 \pm 0.0083$
$\text{H}(\text{D})^{12}\text{C}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	$5323.0717 \pm 0.0130$	$5176.9949 \pm 0.0120$

Table 3. Rotational constant  $A$  (MHz) and distortion constants  $T_1$  and  $T_4$ <sup>a</sup> (kHz) for assumed inertial defects ( $\text{u}\text{\AA}^2$ )  $-0.20$ ;  $0.00$ ;  $+0.20$ , as calculated by ROTFIT.

Molecule	Assumed $\Delta$	$A$	$T_1$	$T_4$
$\text{H}_2^{12}\text{C}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	+0.20	$306027.66 \pm 1.4$	$1.5511 \pm 0.077$	$171.29 \pm 3.6$
	0.00	$272964.15 \pm 0.92$	$0.9100 \pm 0.061$	$172.27 \pm 3.0$
	-0.20	$246348.35 \pm 0.64$	$0.3753 \pm 0.048$	$173.14 \pm 2.4$
$\text{H}_2^{13}\text{C}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	+0.20	$306061.07 \pm 1.3$	$1.4225 \pm 0.066$	$160.03 \pm 3.4$
	0.00	$272990.63 \pm 0.91$	$0.8622 \pm 0.052$	$160.87 \pm 2.9$
	-0.20	$246369.82 \pm 0.63$	$0.3955 \pm 0.042$	$161.62 \pm 2.4$
$\text{H}_2^{12}\text{C}=\text{}^{13}\text{C}=\text{}^{32}\text{S}$	+0.20	$306042.57 \pm 1.3$	$1.5310 \pm 0.069$	$169.95 \pm 3.2$
	0.00	$272976.11 \pm 0.86$	$0.8948 \pm 0.055$	$170.90 \pm 2.6$
	-0.20	$246358.16 \pm 0.61$	$0.3643 \pm 0.045$	$171.75 \pm 2.3$
$\text{H}_2^{12}\text{C}=\text{}^{12}\text{C}=\text{}^{34}\text{S}$	+0.20	$306007.98 \pm 1.4$	$1.4482 \pm 0.074$	$168.87 \pm 4.0$
	0.00	$272948.32 \pm 1.0$	$0.8581 \pm 0.063$	$169.64 \pm 3.5$
	-0.20	$246335.31 \pm 0.78$	$0.3671 \pm 0.055$	$170.29 \pm 3.2$
$\text{H}(\text{D})^{12}\text{C}=\text{}^{12}\text{C}=\text{}^{32}\text{S}$	+0.20	$203873.36 \pm 1.8$	$1.9644 \pm 0.16$	$112.03 \pm 5.4$
	0.00	$188650.89 \pm 1.5$	$1.3462 \pm 0.14$	$113.56 \pm 5.1$
	-0.20	$175543.62 \pm 1.2$	$0.7906 \pm 0.13$	$115.03 \pm 4.8$

<sup>a</sup> As defined by J. Casado, L. Nygaard and G. O. Sørensen, *J. Mol. Struct.* 8 (1971) 211.

exist as intermediates with a life-time  $< ca. 1 - 10$  s as judged by the dimensions of our equipment and an estimated gas flow-rate of 1 ml/s at 10 mTorr. Thus, our present equipment is suitable only for rather long-lived species.

Further, VII (not containing VIII)  $\xrightarrow{1100\text{ K}}$  II (90%) + III (10%) and VIII (not containing VII)  $\xrightarrow{1100\text{ K}}$  III (90%) + II (10%). In both cases carbon "scrambling" definitely takes place. Its extent (10% above) may, however, vary with temperature and the length of the heated zone (here = 20 cm). The available quantity of VII-IX (~5 mg) prevented us from varying these two experimental parameters.

Also, IX  $\xrightarrow{1100\text{ K}}$  IV which shows that suggested mechanisms of reaction must involve hydrogen migration from C(5) to C(4) in VI and/or from C(2) to C(3) in I.

## DISCUSSION

Thiirene (XI, Fig. 3) has been produced by photolysis, isolated in a matrix at 8 K. Its IR spectrum has been recorded.<sup>1,2</sup> Its possible role as an unstable intermediate during the pyrolysis VI  $\xrightarrow{1100\text{ K}}$  I is emphasized by the now well-established carbon scrambling.

$\text{HC}\equiv\text{CSH}$  (ethynyl mercaptan, XII, Fig. 3) is a second possible intermediate. Related  $\text{H}_2\text{C}=\text{CHSH}$  (ethenyl mercaptan, XIV, Fig. 3) which most probably is unstable with respect to thioacetaldehyde,  $\text{CH}_3\text{CSH}$ , has recently been produced by pyrolysis.<sup>13</sup> Provided the life-times of XII and XIV are about equal, XII would have been observed in our experiments if formed in sufficient quantity since, geometrically, XII is close to a symmetric top ( $\chi \sim -0.99$  for reasonable models). Compound XII would, therefore, give rise to strong and easily observable transitions between 18.6 and 40.0 GHz. The fact that such transitions were not seen speaks in favour of XII *not* being an intermediate at  $\text{VI} \xrightarrow{1100\text{ K}} \text{I}$ .

$\text{N}_2\text{S}$  has lately been identified as carrier in an  $\text{N}_2-\text{CS}_2$  laser and reported stable at room temperature.<sup>14</sup> The absence of  $\text{N}_2\text{S}$  in our experiments is in accord with its calculated thermodynamic instability with respect to  $\text{N}_2$  and S. For the process  $\text{N}_2\text{S} \rightarrow \text{N}_2 + \text{S}$  (triplet),  $\Delta G$  (or  $\Delta F$ ) =  $E(\text{N}_2) + E(\text{S}) - E(\text{N}_2\text{S}) + \Delta(pV) - T\Delta S$  ( $E$  for energy,  $p$  for pressure,  $V$  for volume,  $S$  for entropy).  $E(\text{N}_2) + E(\text{S}) - E(\text{N}_2\text{S}) \sim E^\circ(\text{N}_2) + E^\circ(\text{S}) - E^\circ(\text{N}_2\text{S}) = -0.03658$  hartrees ( $E^\circ$  for energy in the hypothetical vibrationless state, available through an *ab initio* estimate (to be published)).

$$E^\circ(\text{N}_2) = -108.77477 \text{ hartrees}$$

$$E^\circ(\text{S}^3\text{P}) = -397.35822 \text{ hartrees}$$

$$E^\circ(\text{N}_2\text{S}) = -506.09641 \text{ hartrees}$$

$$\Delta E^\circ(\text{N}_2\text{S} \rightarrow \text{N}_2 + \text{S}) = -0.03658 \text{ hartrees}$$

which is the value of  $\Delta G$  if  $T\Delta S$  and  $\Delta(pV)$  are ignored.  $T\Delta S > 0$  while  $\Delta(pV)$  is poorly defined in a flow system.

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