The Rotational Spectrum of Monothioformic Acid. III. Dipole Moment and Relative Intensity Measurements[1, 2]

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The molecular electric dipole moment of each of the two planar thiol rotamers of monothioformic acid, in its ground state, has been determined from Stark effect measurements. The results are for *cis*-HC(:O)SH: $\mu_a = 1.805(1)$ D, $\mu_b = 2.228(1)$ D and $\mu = 2.868(1)$ D; whereas for *trans*-HC(:O)SH: $\mu_a = 1.366(1)$ D, $\mu_b = 0.702(1)$ D and $\mu = 1.536(1)$ D. Additional Stark effect measurements on HC(:O)SD and DC(:O)SH have yielded the direction of the dipole moment in each rotamer. The energy difference between the ground vibrational states of *cis*- and *trans*-HC(:O)SH has also been determined by relative intensity measurements. The *cis* rotamer is found to lie at higher energy than the *trans* rotamerb y 2767(7) $\text{J} \cdot \text{mol}^{-1}$ (231.3(6) cm^{-1} or 661.3(17) $\text{cal} \cdot \text{mol}^{-1}$).

I. Introduction

In recent years, microwave spectroscopy has been demonstrated to be an especially powerful technique for studying rotational isomerism. Over 30 molecules have been unequivocally shown to exist in at least two stable rotameric forms through observation of a distinct rotational spectrum for each form[1]. In a few instances the complete molecular structure of each rotamer has been precisely determined through the study of isotopically substituted species[2]. Furthermore, in most cases, Stark effect measurements have yielded accurate electric dipole moment values for each isomer[2, 3]. In the absence of isotopic data these can sometimes play a crucial role in distinguishing one rotamer from the other[3]. There have also been a number of attempts to determine the energy difference between the ground states of rotational isomers by microwave relative intensity measurements[3, 4]. Although the uncertainty in the measured energy differences has usually been rather large, the gradual development of more sophisticated microwave spectrometer systems has now made accurate relative intensity measurements feasible[5–7].

The analysis of the rotational spectra of four isotopic species of monothioformic acid has been previously reported[8, 9]. In each case two abundant isomers were observed. These were identified as the planar *cis* and *trans* rotamers of the thiol form[9]. A preliminary molecular structure was calculated for each rotamer[9].

The first part of the present paper is concerned with the determination of the molecular electric dipole moment exhibited by each of the thiol rotamers of monothioformic acid in its ground vibrational state. Stark effect measurements have been made not only on the parent isotopic species, HC(:O)SH, but also on two isotopically substituted species, HC(:O)SD and DC(:O)SH. The direction of the dipole moment in each rotamer has been deduced from the observed variation in the magnitude of the dipole moment components upon isotopic substitution. The second part of this paper deals with the relative stability of the various isomers of monothioformic acid. Relative intensity and line width measurements in conjunction with the known dipole moment components have yielded an accurate value for the difference in energy between the ground vibrational states of *cis*- and *trans*-HC(:O)SH. A careful, but unsuccessful, search has been made for the possible thione isomers of monothioformic acid.

II. Stark Effect Measurements

The dipole moment studies on monothioformic acid were carried out in the microwave frequency region using a Hewlett-Packard 8460 A MRR spectrometer. Stark shifts were produced by applying a large dc voltage to the septum of the X-band cell. Modulation was achieved by floating a small ac

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voltage, in the form of a 33.333 kHz square wave, on top of the dc signal. The modulated absorption signals were detected using lock-in amplification. Under these conditions each Stark component is split into two lobes which appear with opposite phase on the chart recorder display; one lobe is associated with the off part of the ac voltage, the other with the on part. Since the frequency of only the former was measured, it was not necessary to know accurately the amplitude of the square wave. The dc voltage was monitored using a Hewlett-Packard model 3462 A digital voltmeter. The spacing of the septum in the microwave cell was calibrated by measuring the Stark effect of carbonyl sulfide ($\mu = 0.71521$ D [10]).

The frequency of every Stark component studied was recorded at a number (10 – 20) of different dc voltages. The maximum displacement of the Stark component from the field-free line was typically 25 MHz. Each set of data was then fit, using the least squares procedure, to an expression of the form [11]

$$\nu = a + \beta V^2 + \gamma V^4 \tag{1}$$

where ν is the frequency of the Stark component, V is the dc voltage and α, β and γ are parameters to be determined in the fit. This procedure was applied to both the monothioformic acid and the carbonyl sulfide measurements. In each instance, the γ coefficient was found to be significant but very small, while the α coefficient was always in very good agreement with the frequency of the zero-field line.

Table I. Stark coefficients of monothioformic acid [a].

Species	Transition	$\beta' \times 10^5$
trans-HC(:O)SH	$1_{01}-0_{00}$ $M_J = 0$	2.1866(23) [b]
	$1_{11}-2_{02}$ $M_J = 0$	−0.4795(17)
	$2_{02}-1_{01}$ $M_J = \pm 1$	0.52113(84)
	$2_{12}-3_{03}$ $M_J = 0$	0.15989(59)
trans-HC(:O)SD	$2_{02}-1_{01}$ $M_J = \pm 1$	0.52606(68)
	$1_{11}-2_{02}$ $M_J = 0$	−0.4374(19)
trans-DC(:O)SH	$2_{02}-1_{01}$ $M_J = \pm 1$	0.52099(85)
	$1_{11}-2_{02}$ $M_J = 0$	−0.4154(14)
cis-HC(:O)SH	$1_{01}-0_{00}$ $M_J = 0$	4.0571(45)
	$1_{11}-2_{02}$ $M_J = 0$	0.17584(66)
	$2_{02}-1_{01}$ $M_J = 0$	1.0723(19)
	$2_{12}-3_{03}$ $M_J = 0$	1.4867(32)
cis-HC(:O)SD	$2_{02}-1_{01}$ $M_J = \pm 1$	1.1654(36)
	$1_{11}-2_{02}$ $M_J = 0$	0.2374(15)
cis-DC(:O)SH	$2_{02}-1_{01}$ $M_J = \pm 1$	1.0554(22)
	$1_{11}-2_{02}$ $M_J = 0$	0.8116(19)

[a] β' has units of MHz/(Volt/cm)^2. $\beta' = \beta \cdot d^2$.
[b] The numbers in parentheses are standard errors.

The β coefficient determined from the measurements on carbonyl sulfide was used to determine the cell constant [11], d. The β coefficients of the various monothioformic acid Stark components, scaled by the cell constant squared, are reported in Table I. Figure 1 shows a plot of ν vs the square of the electric field strength, $\mathcal{E} = V/d$, for the $M_J = \pm 1$ Stark component of the $2_{02} - 1_{01}$ transition of *trans*-HC(:O)SH. The effect of the quartic term is so slight that it is not discernable on this plot.

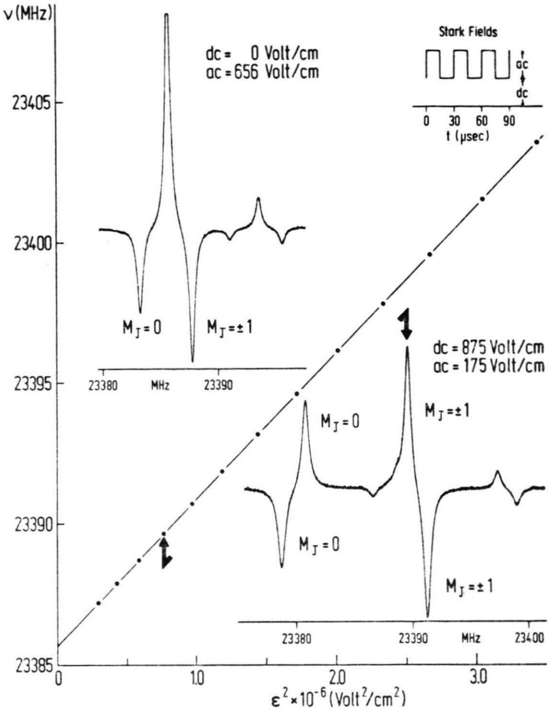

Fig. 1. Frequency of the $M_J = \pm 1$ Stark component of the $2_{02} - 1_{01}$ transition of *trans*-HC(:O)SH plotted against the square of the electric field strength, ε. The inserts show this transition under two different modulation conditions.

The second order Stark effect energy, $[W_S^{(2)}]_{J\tau M_J}$, of an asymmetric rotor molecule is related to the molecular electric dipole moment by the equation [12, 13]

$$\begin{aligned}[W_S^{(2)}]_{J\tau M_J} = \sum_i \frac{\mu_i^2\,\mathcal{E}^2}{2J+1} & \\ \times \sum_{\tau'}{}' \Bigg[& \frac{J^2 - M_J^2}{J(2J-1)} \, \frac{{}^iS_{J\tau,\,J-1\tau'}}{W^0_{J\tau} - W^0_{J-1\tau'}} \\ & + \frac{M_J^2}{J(J+1)} \, \frac{{}^iS_{J\tau,\,J\tau'}}{W^0_{J\tau} - W^0_{J\tau'}} \\ & + \frac{(J+1)^2 - M_J^2}{(J+1)(2J+3)} \, \frac{{}^iS_{J\tau,\,J+1\tau'}}{W^0_{J\tau} - W^0_{J+1\tau'}} \Bigg]\end{aligned} \tag{2}$$

where μ_i is the component of the dipole moment along the a, b or c principal axis and J and M_J are quantum numbers for the total rotational angular momentum and its projection along the space fixed direction respectively. The ${}^iS_{J\tau,J'\tau'}$ are line strength factors and the $(W^0_{J\tau} - W^0_{J'\tau'})$ are energy differences between the unperturbed rotational levels designated by $J\tau$ and $J'\tau'$ respectively.

The quadratic Stark coefficients reported in Table I were analysed using Eq. (2) to obtain values of μ_a and μ_b for the *cis* and *trans* rotamers of HC(:O)SH, DC(:O)SH and HC(:O)SD. In each case, μ_c was presumed to be zero since it is known that both rotamers are planar[9]. The required line strength factors and energy differences were calculated from the published spectroscopic constants[8, 9]. No attempt was made to account for polarizability effects[11] which are believed to be smaller than the experimental error in the present work. The results are presented in Table II.

Table II. The dipole moment of monothioformic acid [a].

Species	μ_a	μ_b	μ
trans-HC(:O)SH	1.366(1)	0.702(1)	1.536(1)[b]
trans-HC(:O)SD	1.361(1)	0.726(4)	1.542(2)
trans-DC(:O)SH	1.353(1)	0.727(3)	1.536(2)
cis-HC(:O)SH	1.805(1)	2.228(1)	2.868(1)
cis-HC(:O)SD	1.862(3)	2.185(3)	2.870(3)
cis-DC(:O)SH	1.768(2)	2.264(2)	2.873(2)

[a] Dipole moment measured in Debye.

[b] The numbers in parentheses are standard errors.

III. Electric Dipole Moment Directions

Stark effect measurements yield very precisely the magnitude of dipole moment components but provide no direct information as to their sign. The direction of the dipole moment can frequently be deduced, however, by arguments based on the semi-quantitative concepts of electronegativity and bond moments. In addition, the isotopic dependence of the magnitude of the dipole moment components can in some instances be used to specify unambiguously the axis along which the total dipole moment lies[2]. All of these approaches are used together in the following discussion to show that the dipole moments of *cis*- and *trans*-HC(:O)SH have the directions indicated in Figure 2. Throughout this discussion the arrow heads indicate the positive end of the dipole moment.

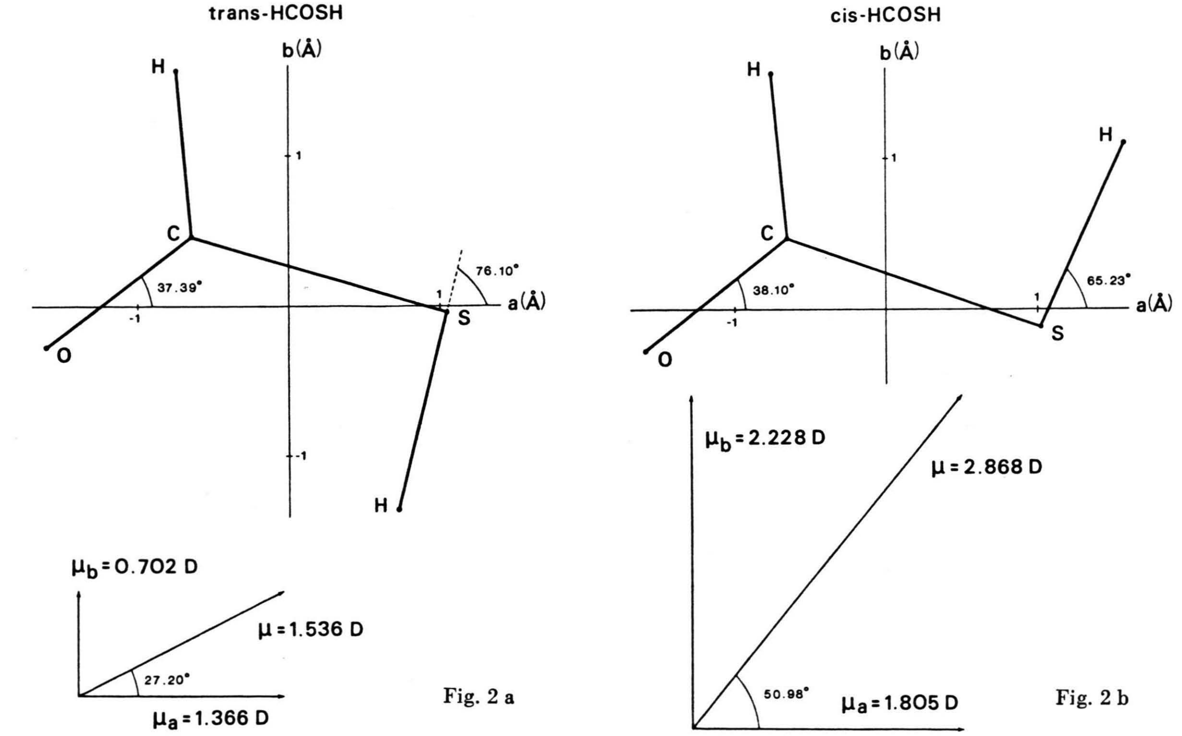

Fig. 2 a

Fig. 2 b

Fig. 2. Molecular structures and electric dipole moments of the two abundant isomers of monothioformic acid.

Consider first the direction of the dipole moment in the *cis* rotamer. There are two possibilities for the orientation of the total dipole moment relative to the molecular frame: (I) inclined at an angle of 12.9° to the CO bond, (II) inclined at an angle of 89.1° to the CO bond. It was possible to distinguish between these two cases by making Stark effect measurements on the deuterium substituted isotopic species. The dipole moment components change slightly in magnitude on isotopic substitution primarily due to a rotation of the principal axis system. With the assumption that this was the only cause of such changes, the magnitude of the components in *cis*-HC(:O)SD and in *cis*-DC(:O)SH was calculated for both cases from the measured dipole moment of *cis*-HC(:O)SH and the published molecular structure[9]. The results are compared in Table III with the measured components and clearly show that orientation (I) is the correct one. Furthermore, since both electropositive hydrogen atoms lie on one side of the *a*-axis and the electronegative oxygen atom on the other side, the only reasonable polarity for the *b*-component, and hence the total dipole moment, is that indicated in Figure 2.

Table III. Direction of the dipole moment in *cis*-HC(:O)SH [a].

Species	μ_i	I [c]	II [d]	Observed
HC(:O)SD	μ_a	1.855	1.755	1.862 (3) [b]
	μ_b	2.187	2.268	2.185 (3)
DC(:O)SH	μ_a	1.770	1.841	1.768 (2)
	μ_b	2.257	2.199	2.264 (2)

[a] Dipole moment measured in Debye.
[b] The numbers in parentheses are standard errors.
[c] Calculated assuming that μ is inclined at an angle of 12.9° to the CO bond in *cis*-HC(:O)SH.
[d] Calculated assuming that μ is inclined at an angle of 89.1° to the CO bond in *cis*-HC:O)SH.

Table IV. Direction of the dipole moment in *trans*-HC(:O)SH [a].

Species	μ_i	I [c]	II [d]	Observed
HC(:O)SD	μ_a	1.357	1.375	1.361 (1) [b]
	μ_b	0.720	0.684	0.726 (4)
DC(:O)SH	μ_a	1.355	1.377	1.353 (1)
	μ_b	0.724	0.681	0.727 (3)

[a] Dipole moment measured in Debye.
[b] The numbers in parentheses are standard errors.
[c] Calculated assuming that μ is inclined at an angle of 10.2° to the CO bond in *trans*-HC(:O)SH.
[d] Calculated assuming that μ is inclined at an angle of 64.6° to the CO bond in *trans*-HC(:O)SH.

The orientation of the dipole moment in the *trans* rotamer was also determined by investigating the isotopic dependence of the dipole moment components. Exactly the same procedure was followed as that described above for the *cis* rotamer. The results are collected in Table IV and again they clearly show that the correct orientation is the one in which the dipole moment roughly parallels the CO bond. Electronegativity arguments then suggest that the most likely polarity of the dipole moment along this axis is that indicated in Figure 2.

The substantial difference between the dipole moments of *cis*- and *trans*-HC(:O)SH may be semiquantitatively accounted for by vector addition of bond moments. The total dipole moment in both rotamers is resolved into a frame moment, $\boldsymbol{\mu}_F$, and a sulfur-hydrogen bond moment, $\boldsymbol{\mu}_{SH}$. It is assumed that: (i) the $\boldsymbol{\mu}_F$ moment has the same magnitude and direction in the two rotamers, (ii) the $\boldsymbol{\mu}_{SH}$ moment has the same magnitude and opposite direction in the two rotamers. These assumptions can not be completely correct since it is known that the structure of *cis*-HC(:O)SH differs sightly from that of *trans*-HC(:O)SH, and further, that the HSC angle is slightly larger than 90° in both rotamers[9]. It is expected, however, that they are reasonably good approximations. The results summarized in Fig. 3 are then obtained if the total dipole moment of each rotamer is taken to have its previously determined magnitude and direction. The calculated sulfur-hydrogen bond moment (0.794 D) is similar in magnitude to the dipole moment of the SH radical

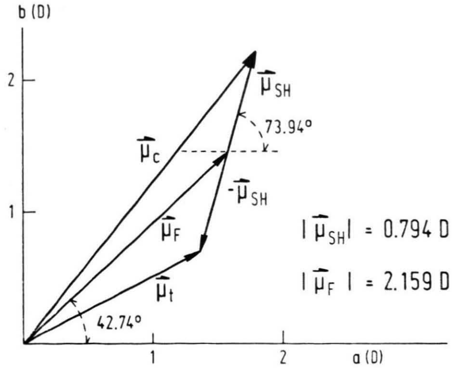

Fig. 3. Resolution of the total dipole moments of *cis*-HC(:O)SH, $\boldsymbol{\mu}_c$, and *trans*-HC(:O)SH, $\boldsymbol{\mu}_t$, into a frame moment, $\boldsymbol{\mu}_F$, and a sulfur-hydrogen bond moment, $\boldsymbol{\mu}_{SH}$.

(0.7580 D [14]). It is also consistent with the sulfur-hydrogen bond moments reported for H_2S (0.71 D), $HCCCH_2SH$ (0.79 D) and CH_3SH (1.10 D) by Mirri, Scappini, and Mäder [15].

IV. Relative Intensity Measurements

The relative intensity of two absorption lines due to the same rotational transition in the two different rotamers of HC(:O)SH is given by [5, 6, 13]

$$\frac{\gamma_c^0}{\gamma_t^0} = \left(\frac{f_c}{f_t}\right)\left(\frac{\nu_c}{\nu_t}\right)^2\left(\frac{\Delta\nu_t}{\Delta\nu_c}\right)\left(\frac{|\mu_{ij}|_c^2}{|\mu_{ij}|_t^2}\right) e^{-\Delta W_r/kT} \qquad (3)$$

where the subscripts c and t denote *cis* and *trans* respectively and:

γ^0 = the intensity coefficient at maximum absorption of the narrow pressure-broadened absorption line in the limit of low microwave power.

f = the fraction of molecules in the ground vibrational state of the *cis* or *trans* rotamer.

ν = the resonance frequency of the rotational transition.

$\Delta\nu$ = the line-width of the rotational transition.

$|\mu_{ij}|^2$ = the square of the dipole moment matrix element connecting the two rotational states of the transition.
= $\mu_i^2 \cdot {}^iS_{J\tau, J'\tau'}/(2J+1)$, where μ_i is the component of the dipole moment active in the transition (μ_a or μ_b).

ΔW_r = the difference in the rotational energy of the lower level involved in the transition for the two rotamers (*cis-trans*).

k = Boltzmann constant.

T = absolute temperature.

In previous studies of the energy difference between rotational isomers it has usually been assumed that the appropriate line-width ratios were unity [3, 16]. This is certainly not the case in the present instance. Figure 4 shows that *cis*-HC(:O)SH has much broader absorption lines than *trans*-HC(:O)SH. Thus in order to determine accurately the ratio f_t/f_c it was necessary to measure $\Delta\nu_t/\Delta\nu_c$ as well as γ_t^0/γ_c^0. An analysis similar to that reported here has very recently been carried out by Varma and Curl [17] on nitrous acid, HONO, which also exists as *cis* and *trans* rotamers.

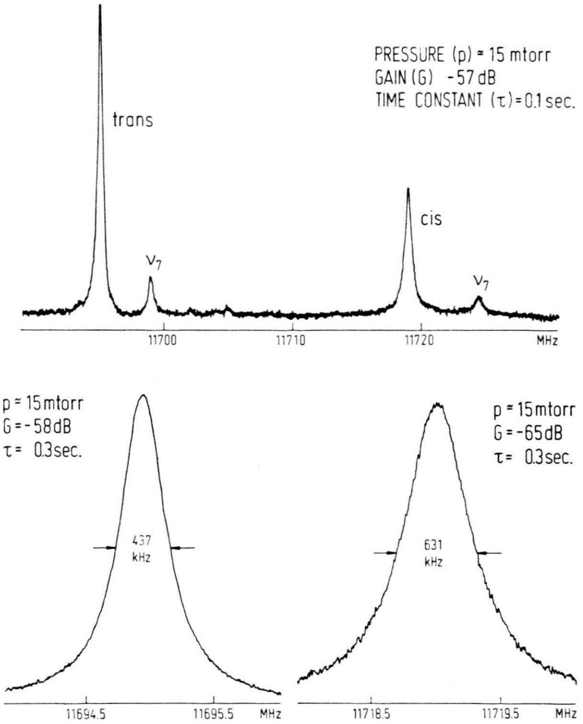

Fig. 4. Relative intensity and line-widths of the $1_{01}-0_{00}$ transitions of *trans*- and *cis*-HC(:O)SH. The upper trace shows a survey scan in the region of the $1_{01}-0_{00}$ transitions. The lower trace shows the line profile of this transition for the two rotamers under higher resolution.

Relative intensity measurements were made on five transitions of HC(:O)SH using the Hewlett-Packard 8460 A MRR spectrometer. This instrument is equipped with a bridge-arm system in the P- and K-band spectral regions. Four of the five transitions investigated fall in one or the other of these bands. The measurements on these four were made with microwave power in the Stark cell attenuated to a level 20 dB below that required to saturate the absorption signal, while power in the bridge arm was adjusted to maintain a constant detector crystal current of 100 μA. The fifth transition ($1_{01}-0_{00}$) falls in X band where no bridge system is available. Relative intensity measurements were made on this transition at low detector crystal current levels with power in the Stark cell ~10–15 dB below that required to saturate the transition.

The line-widths and the peak intensity coefficient ratios of the absorption signals were determined from the same set of measurements. Each line was recorded on chart paper by linearly sweeping the source frequency across the absorption signal profile. The full-width at half-height and peak intensity of the absorption line were then read directly off the

Table V. Relative intensity measurements on *cis*- and *trans*-HC(:O)SH.

Transition	T (°K)	p [a]	γ_t^0/γ_c^0	$\Delta\nu_t$ [b] [kHz]	$\Delta\nu_c$ [b] [kHz]	$(\nu_c/\nu_t)^2$	$\lvert\mu_{ij}\rvert_c^2/\lvert\mu_{ij}\rvert_t^2$	$e^{-\Delta W_r/kT}$	f_t/f_c	ΔE [c] [cm^{-1}]
$1_{01}-0_{00}$	299.6	13	2.460	365	520	1.00412	1.7468	1.0000	3.029	230.7
	299.6	15	2.455	397	570	1.00412	1.7468	1.0000	2.999	228.7
$2_{02}-1_{01}$	299.3	13	2.480	320	455	1.00413	1.7468	1.0000	3.060	232.6
	299.3	15	2.515	385	550	1.00413	1.7468	1.0000	3.088	234.6
$2_{11}-1_{10}$	299.3	11	2.600	295	445	1.00351	1.7468	0.99986	3.021	230.0
	299.3	12	2.573	320	475	1.00351	1.7468	0.99986	3.038	231.1
$6_{06}-5_{15}$	299.9	13	0.5146	310	482	0.915526	10.047	0.99979	3.044	232.0
	300.3	15	0.5140	355	557	0.915526	10.047	0.99979	3.013	230.2
	300.3	21	0.5224	480	770	0.915526	10.047	0.99979	2.995	228.9
$29_{2,28}-28_{3,25}$	299.3	13	0.6815	320	550	0.761396	10.251	0.99734	3.086	234.4

[a] Approximate in mTorr. [b] Full-width at half-height. [c] $\Delta E = E_c - E_t$.

chart paper. In order to circumvent a slight (less than 3% in 10 minutes) sample decay problem, the stronger of the two absorption lines for each transition was recorded twice at equally spaced intervals before and after observation of the weaker line. An average of the two sets of measurements on the stronger line was then taken.

The results of the relative intensity measurements on HC(:O)SH are presented in Table V. The experimental uncertainty in the line-width and peak intensity coefficient ratio values is estimated to be less than 2%. This is consistent with the observed variation in the calculated values of f_t/f_c. Also reported in Table V are values for the energy difference between the ground vibrational states of the *cis* and *trans* rotamers. These were calculated from the f_t/f_c numbers using the Boltzmann equation

$$\Delta E = E_c - E_t = k\,T \ln(f_t/f_c)\,, \tag{4}$$

with the implicit assumption that the equilibrium

$$trans\text{-HC(:O)SH} \rightleftharpoons cis\text{-HC(:O)SH} \tag{5}$$

had been established. The average of the ΔE values reported in Table V is 231.3(6) cm^{-1} (or 661.3(17) cal·mol^{-1} or 2767(7) J·mol^{-1}), where the number in parenthesis is one standard error.

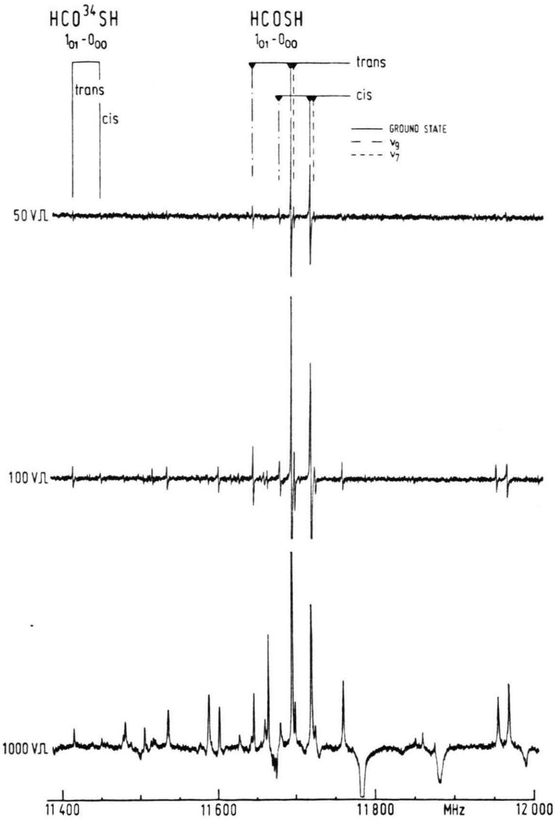

Fig. 5. Survey spectrum of monothioformic acid from 11.4–12.0 GHz at three different Stark voltages. The various $1_{01}-0_{00}$ transitions are labelled and are distinguished by their fast Stark effect.

V. Discussion

The microwave spectrum of monothioformic acid in the frequency region 11.4 – 12.0 GHz is shown in Fig. 5 at three different Stark voltages. Absorption lines due to the $1_{01}-0_{00}$ transition of the *cis* and *trans* rotamers of HC(:O)SH in their ground states and in the two lowest lying excited vibrational states have been identified. The observed satellite lines are due to excitation of the SH-torsional mode ($\nu_9 =$ 384 cm^{-1} for the *cis*, and 300 cm^{-1} for the *trans* rotamer), and the OCS-bending mode ($\nu_7 = 430$ cm^{-1}

for both rotamers)[18]. The next higher vibrational frequency falls above 650 cm^{-1} and no satellite lines due to this or higher frequency vibrations have been observed. Also labelled in Fig. 5 are lines due to the $1_{01} - 0_{00}$ transition in the ground states of *cis*- and *trans*-HC(:O)^{34}SH. All of these transitions are easily distinguished from the higher-*J* transitions which fall in this frequency region by their large Stark effect. At the lowest Stark field they are the only transitions which are sufficiently modulated to be clearly observable.

The gaseous sample of monothioformic acid whose spectrum is shown in Fig. 5 is presumed to have consisted of an equilibrium mixture of the thiol and thione isomers. This seems likely since it is known that the sulfur hydrogen atom of the thiol rotamers is quite labile[9]. On the other hand, the opposite situation has been shown to exist for the methyl ester of monothioformic acid: the thiol[19] ($HC(:O)SCH_3$) and thione[20] ($HC(:S)OCH_3$) isomers have both been isolated and characterized. In each case only the rotamer with the methyl group *trans* to the carbon hydrogen atom was observed.

Trial rigid rotor calculations based on assumed structural parameters predict that the $1_{01} - 0_{00}$ transitions of *cis*- and *trans*-HC(:S)OH should also lie near 11.7 GHz. Like the $1_{01} - 0_{00}$ transitions of the thiol rotamers, these transitions are expected to have a relatively large second order Stark effect and hence to be more easily modulated than most higher-*J* transitions. A thorough search of the 11.0 – 12.4 GHz frequency region failed to turn up any likely candidates for the $1_{01} - 0_{00}$ transition of either of the thione rotamers. Since the absorption lines due to HC(:O)^{34}SH in natural isotopic abundance are clearly visible it is inferred that 4% is an upper limit on the amount of HC(:S)OH present in gaseous monothioformic acid at room temperature.

Randhawa and Rao[21] have recently made a theoretical study of isomerism in monothioformic acid using the extended Hückel and CNDO/2 methods. Their findings were inconclusive: the extended Hückel calculation gave *cis*-HC(:O)SH as the lowest energy form while the CNDO/2 calculation predicted thas *cis*-HC(:S)OH would be the most stable isomer. Both results are, of course, incompatible with our experimental findings.

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